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Supporting Information

Triethylamine-Methanol Mediated Selective Removal of Oxophenylacetyl Ester in Saccharides

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[d] *CSIR-Traditional Knowledge Digital Library (TKDL) 14-Satsang Vihar, Vigyan Suchna Bhawan, New Delhi-110067*

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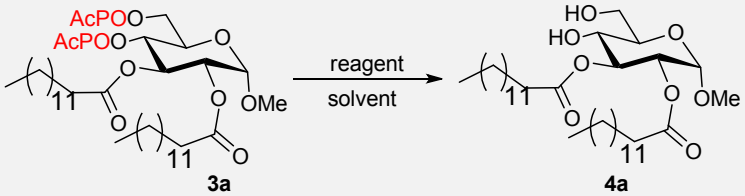
Optimization Table for Lipids protected saccharides



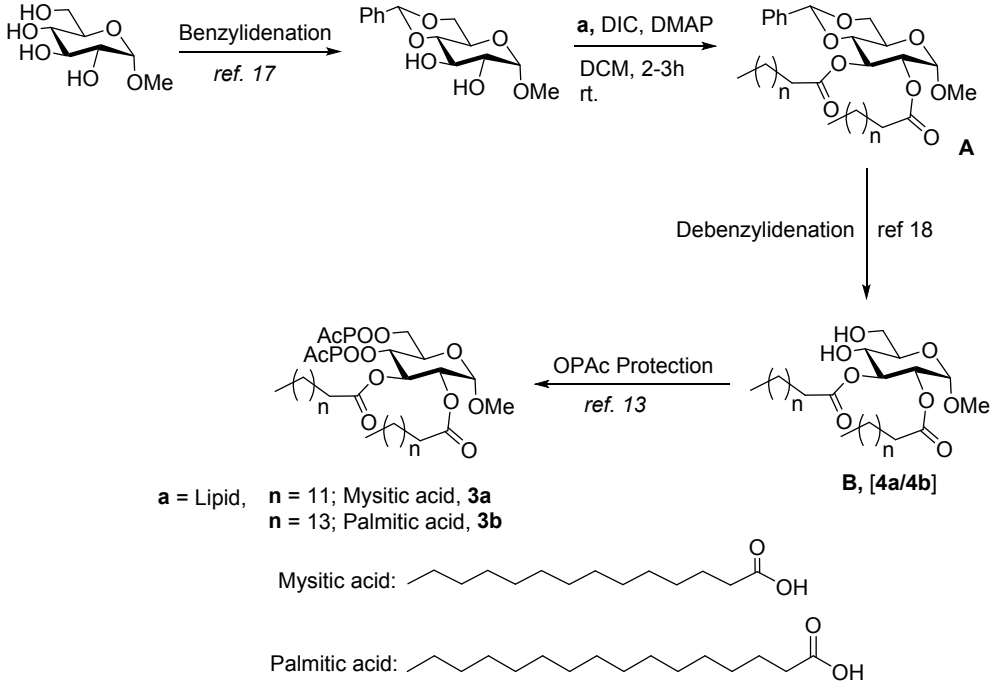
3a **4a**

entry	reagent (mmol)	Time (min)	solvent	Yield(%) **4a**
1	TEA (0.3)	90	MeOH	27
2	TEA (0.3)	180	MeOH	29
3	TEA (0.3)	90	MeOH:DCM (9:1)	72
4	TEA (0.3)	90	MeOH:DCM (8:2)	93
5	TEA (0.3)	90	MeOH:DCM (7:3)	92
Reaction condition: **3** (1 mmol), TEA (0.3 mmol) in 3 mL of MeOH:DCM (8:2) at rt for 90 min.				

1. General synthetic procedure for **3a** and **3b:**

The benzylidenation of α-D-methyl glucose was carried according as per the literature report[17.] The bezylidenated product was dissolved in dry DCM and lipid **(**mystic acid, palmitic acid, and Oelic acid, 2. 0 equiv), DIC (2.1 equiv) and DMAP (2.1 equiv) was added and stirred at room temperature for 3 h in an inert atmosphere. After the reaction was completed as monitored by TLC, the solvent was evaporated in vacuum. After extraction with ethyl acetate and 0.1 N HCl (2-3 washings) followed by $NaHCO_3$ wash the organic layer was collected and dried over anhydrous Na_2SO_4. The residue thus obtained was subjected to column chromatography to give the benzylidenated product **A** which was further subjected to benzylidene removal according to the known procedure[18] to afford **B** (**Scheme 1**). **B** was transformed into the final products (**3a/3b)** as per the literature report.[13]

Scheme 1:



2. General synthetic procedure for **3c** and **3d:**

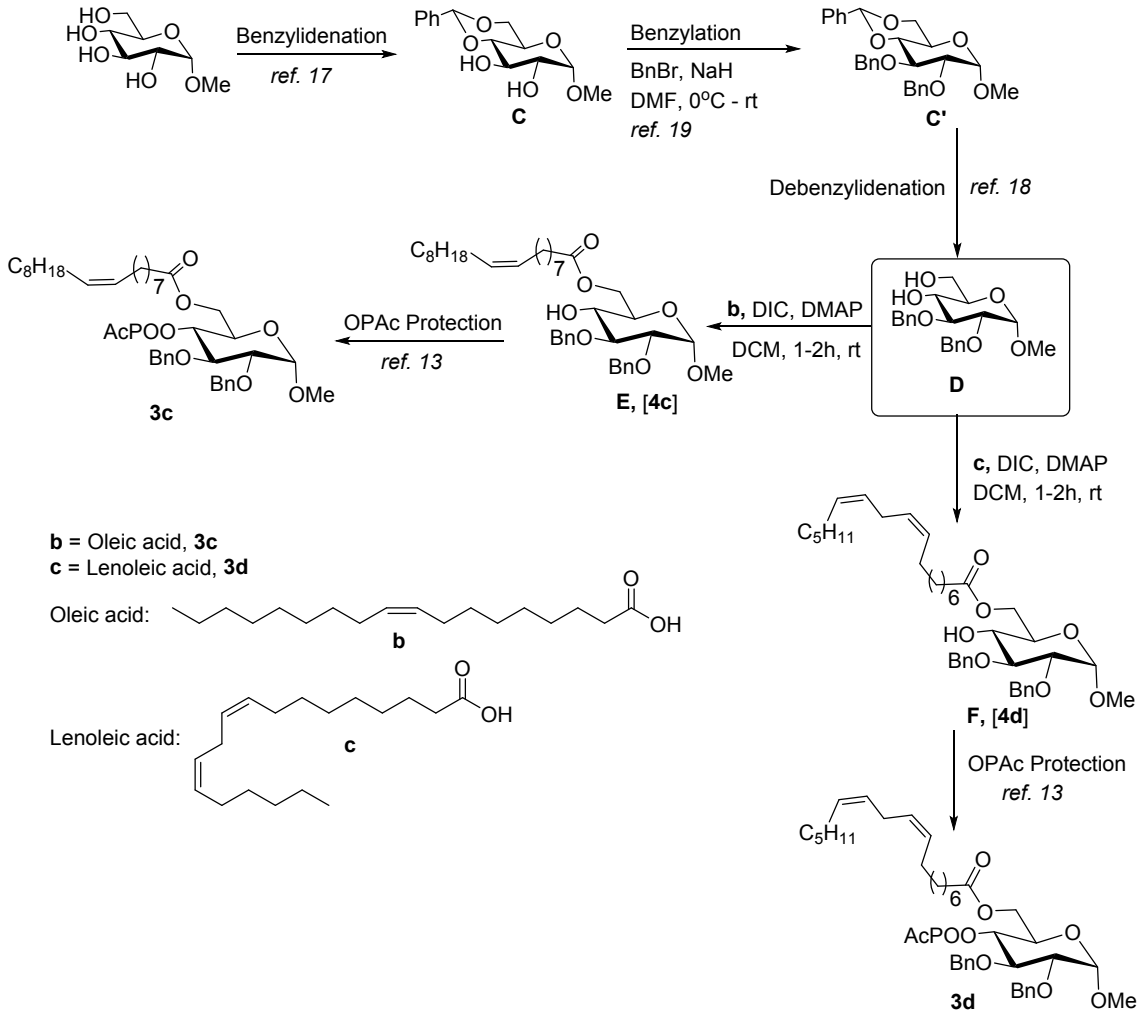
The benzylidenation of α-D-methyl glucose was carried according to the literature report.[17] Benzylation of the bezylidenated product **C** was carried according to the known protocol[19] by using benzylbromide (2 eq.), NaH (2eq.) in DMF at 0^{o}C at rt (35^{o}C) for 3 h. After the reaction was over, NaH was quenched with ice chilled water or MeOH and extracted with ethyl acetate. The organic layer was collected and dried in vacuum. The residue thus obtained was subjected to column chromatography to give the benzylated product **C'** which was further subjected to debenzylidenation according to the known report[18] to afford **D** (**Scheme 2**).

D was transformed into the lipidated saccharide **E** by adding oleic acid **b** (0.9 equiv), DIC (1.0 equiv) and DMAP (1.0 equiv) in DCM and stirred at room temperature for 3 h under N_2 atmosphere. After the reaction was over, the solvent was evaporated in vacuum. After extraction with ethyl acetate and 0.1N HCl (2-3 washings) followed by $NaHCO_3$ wash, the organic layer was collected and dried on Na_2SO_4.

The residue thus obtained was subjected to column chromatography to give lipidated saccharide **E** which was further transformed into the final product **3c** as per the literature report.[13]

Similarly, the synthesis of **3d** was performed by using dissolving linoleic acid **c** (0.9 equiv) in DCM then, DIC (1.0 equiv) and DMAP (1.0 equiv) was added and the reaction mixture was stirred at room temperature for 3h under N_2 atmosphere to yield **F** as gummy solid which was transformed to **3d** according to the known procedure (**Scheme 2**).

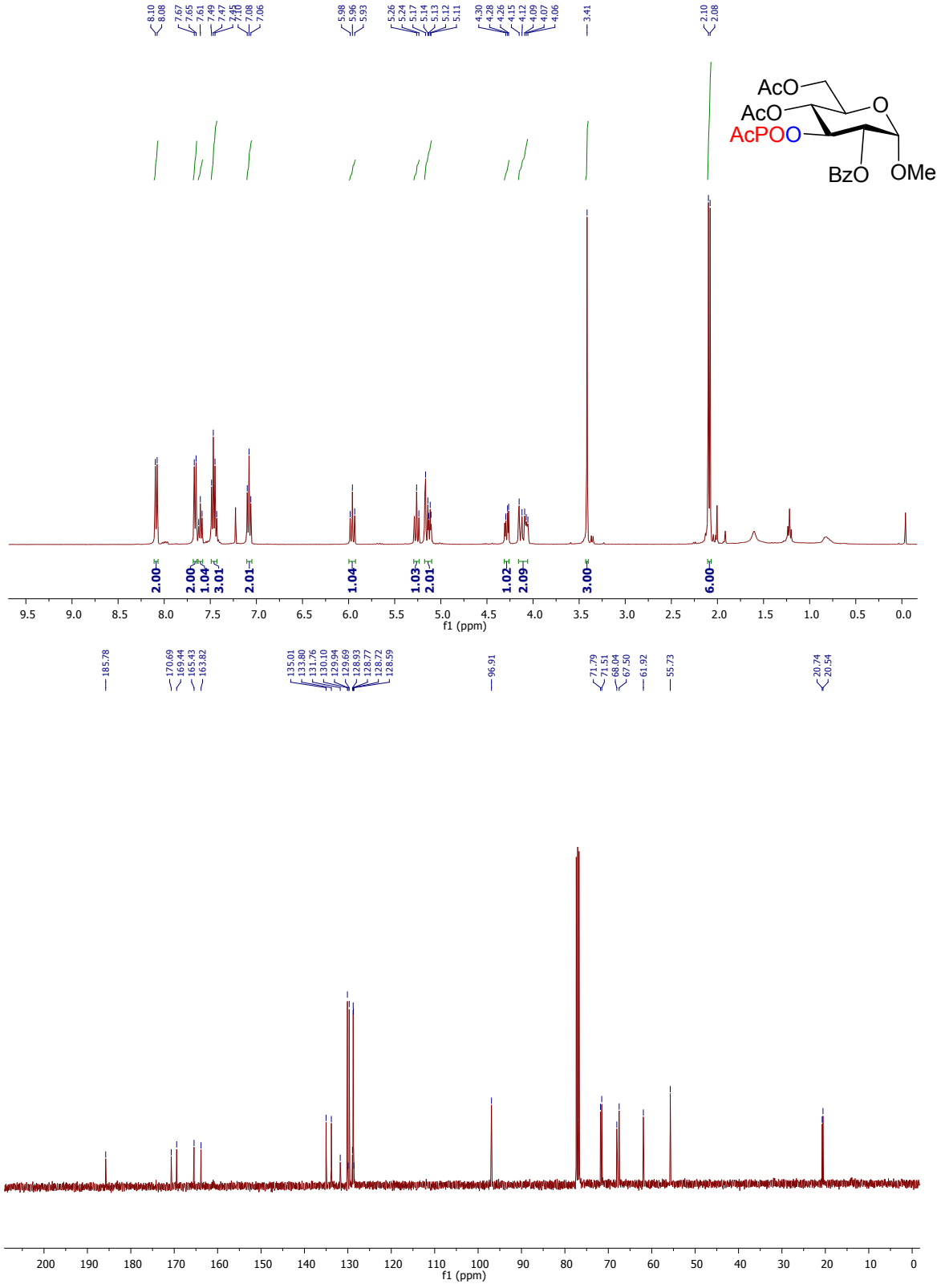
Scheme 2:

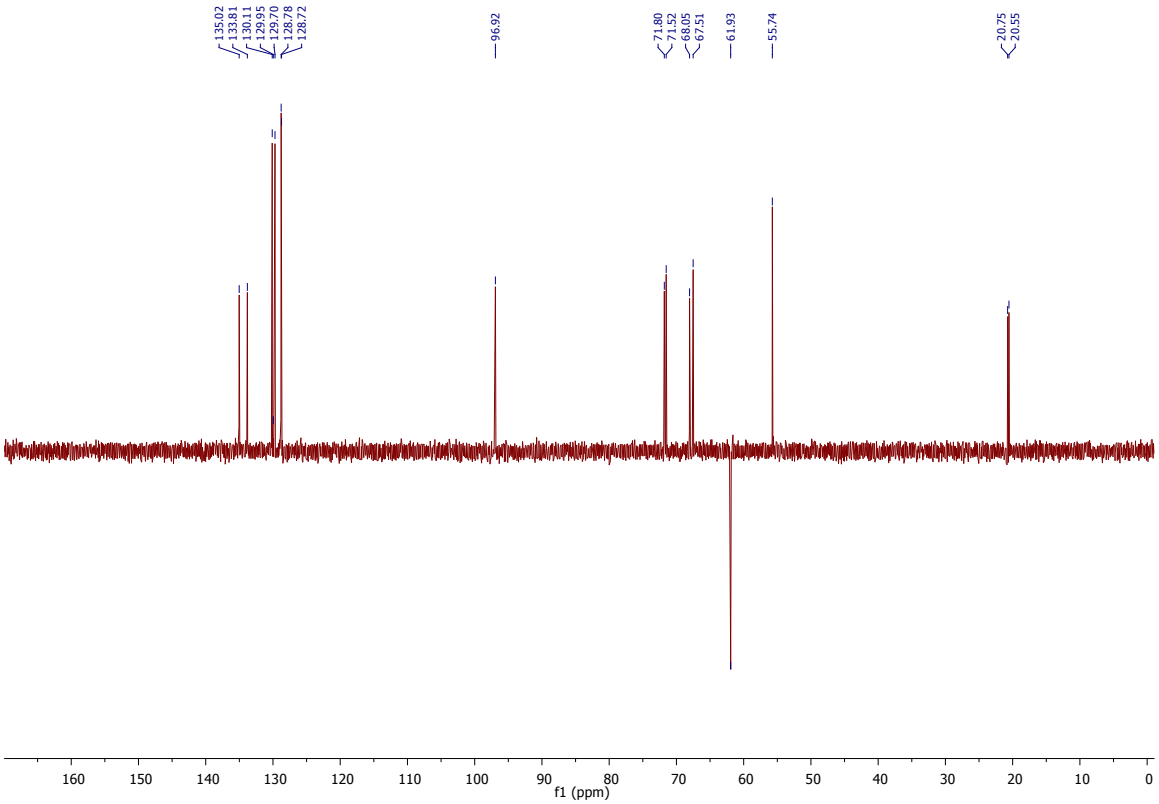


17. M. E. Evans, *Carbohydr. Res.* **21**, 473 **(1972).**
18. J. Xia and Y. Hui, *Synthetic Communications*, 26 (5), 88 1-886 (1996).
19. S. P. Ali and N. K. Jalsa, *Journal of Carbohydrate Chemistry*, 33,185–196, 2014.

3. 3e was synthesized according to the literature report.[13]

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1a ($CDCl_3$)





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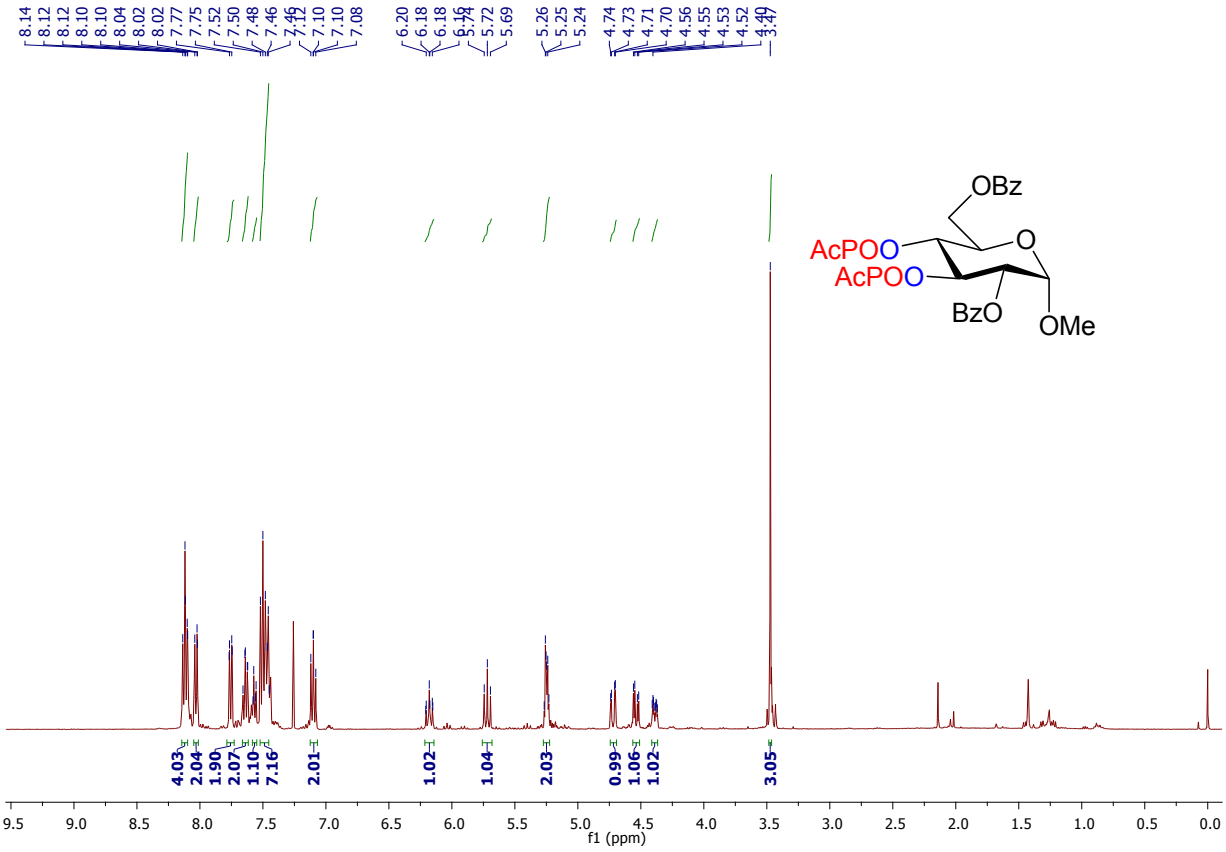

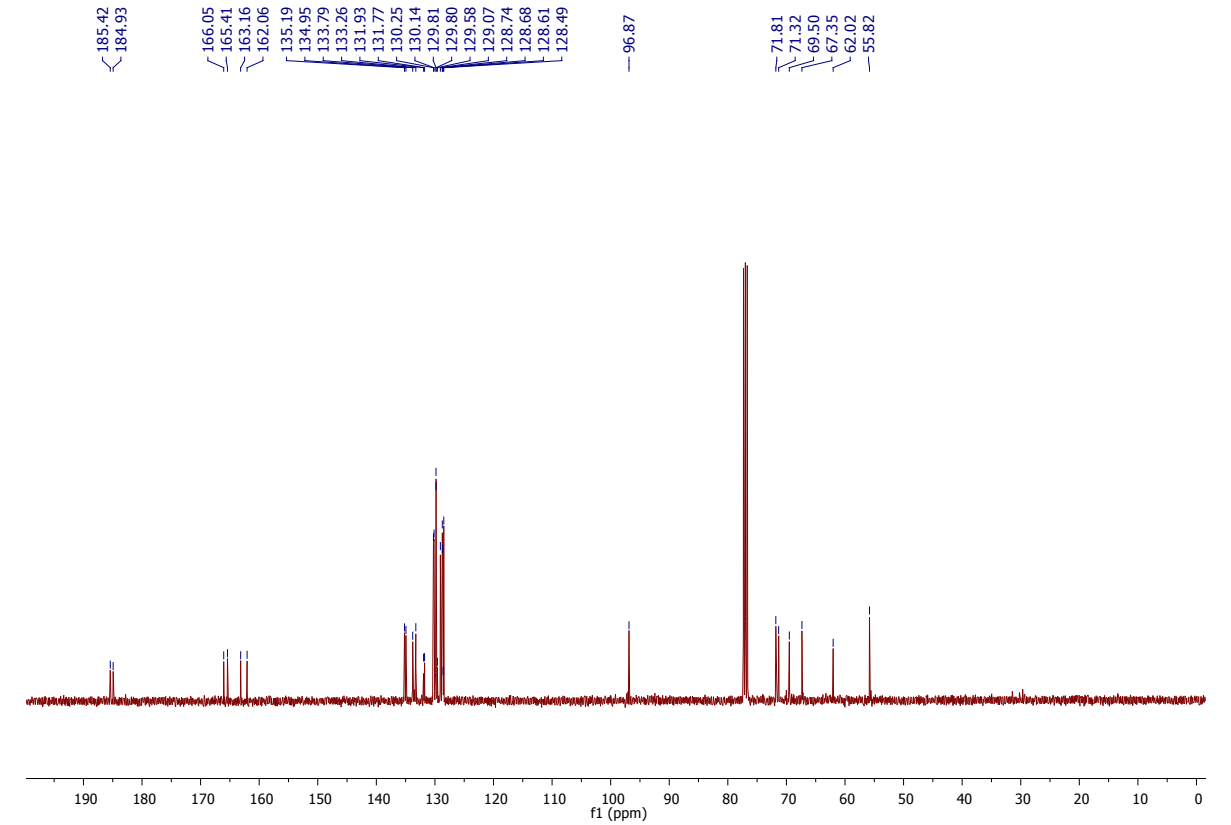
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129.07
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128.61
128.49
96.87
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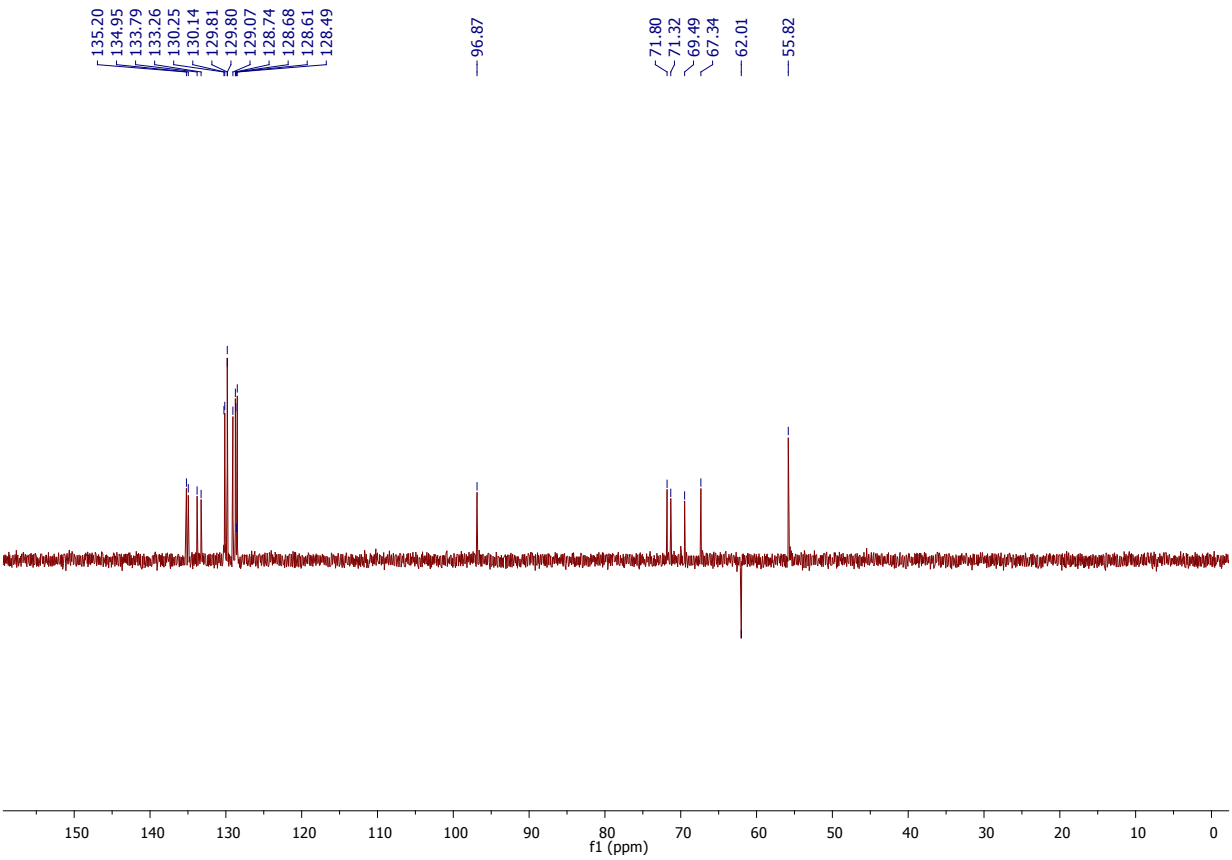
f1 (ppm)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67.34
62.01
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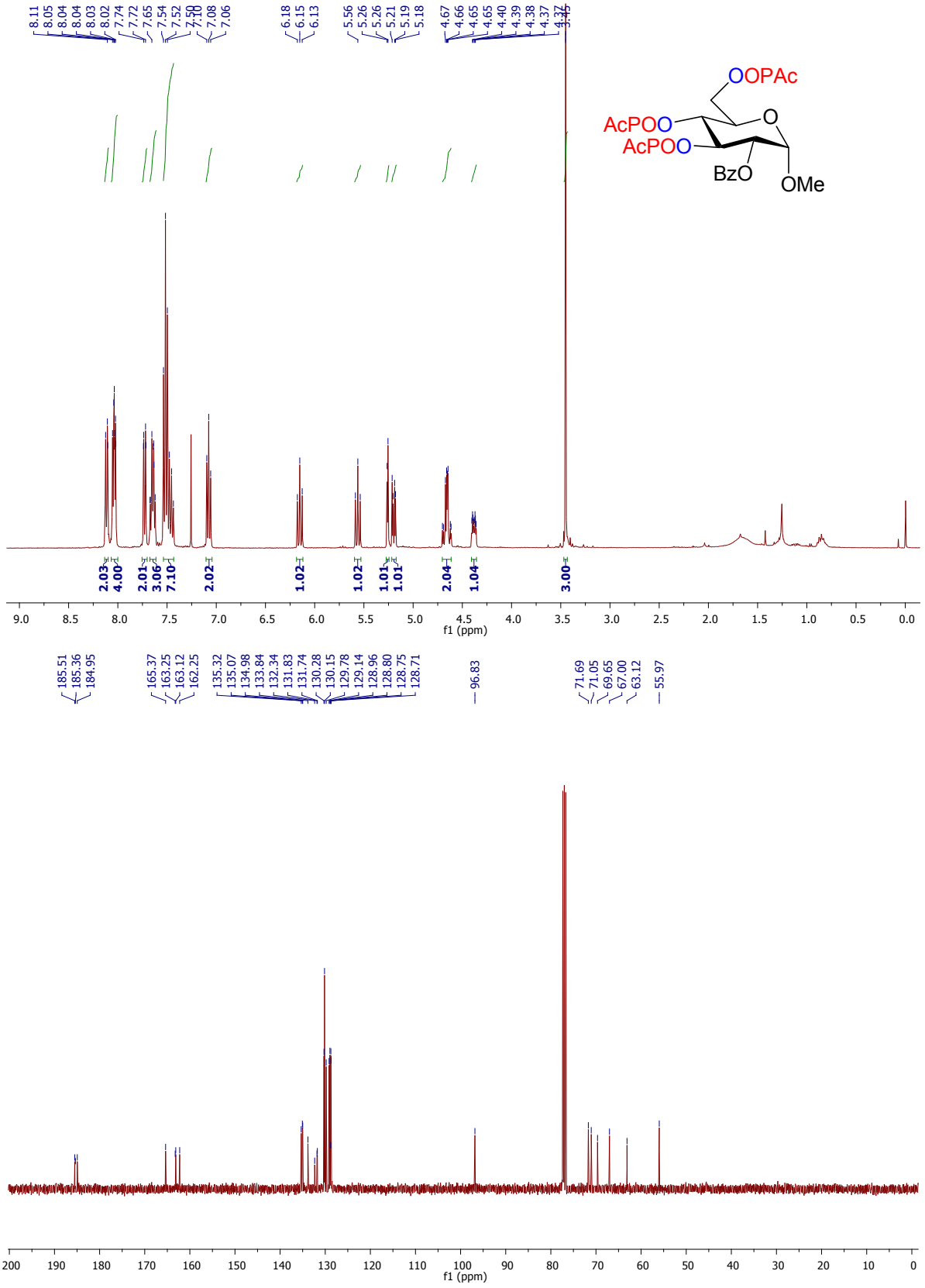
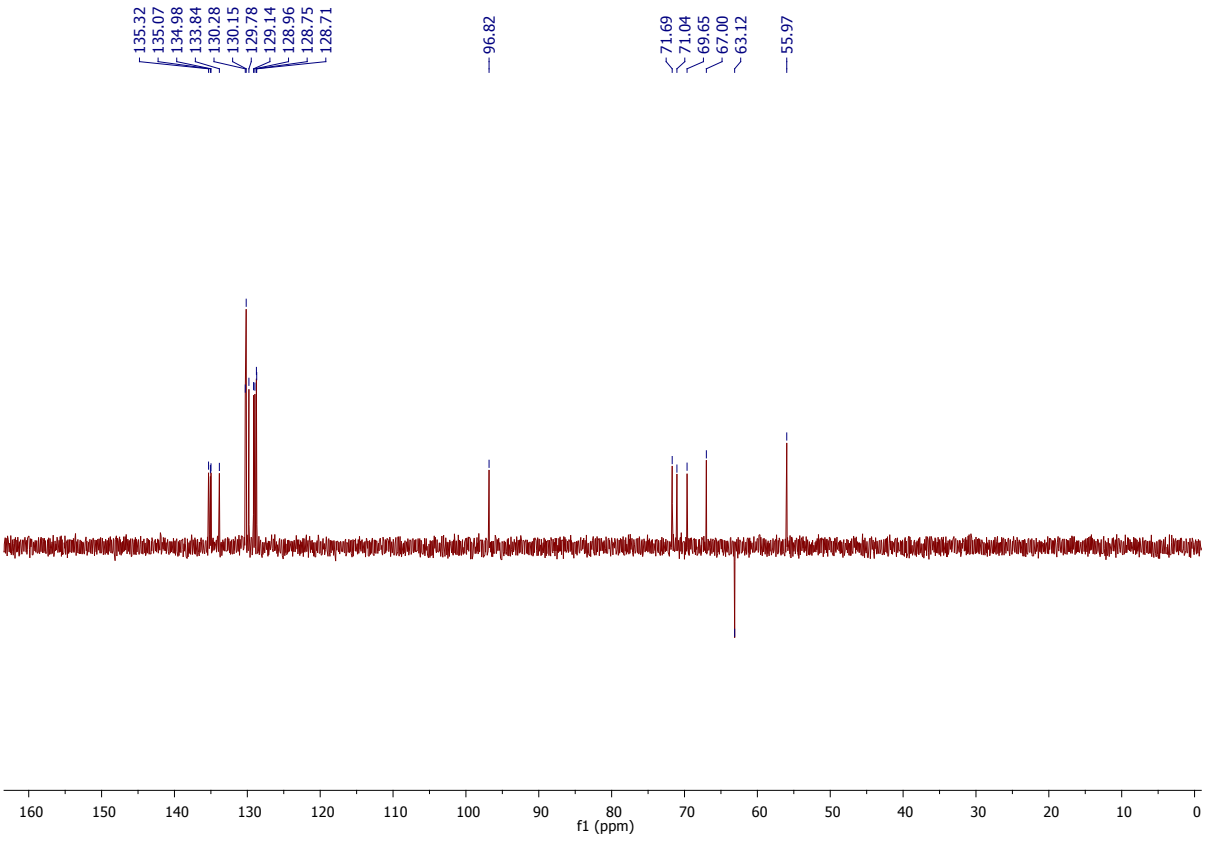
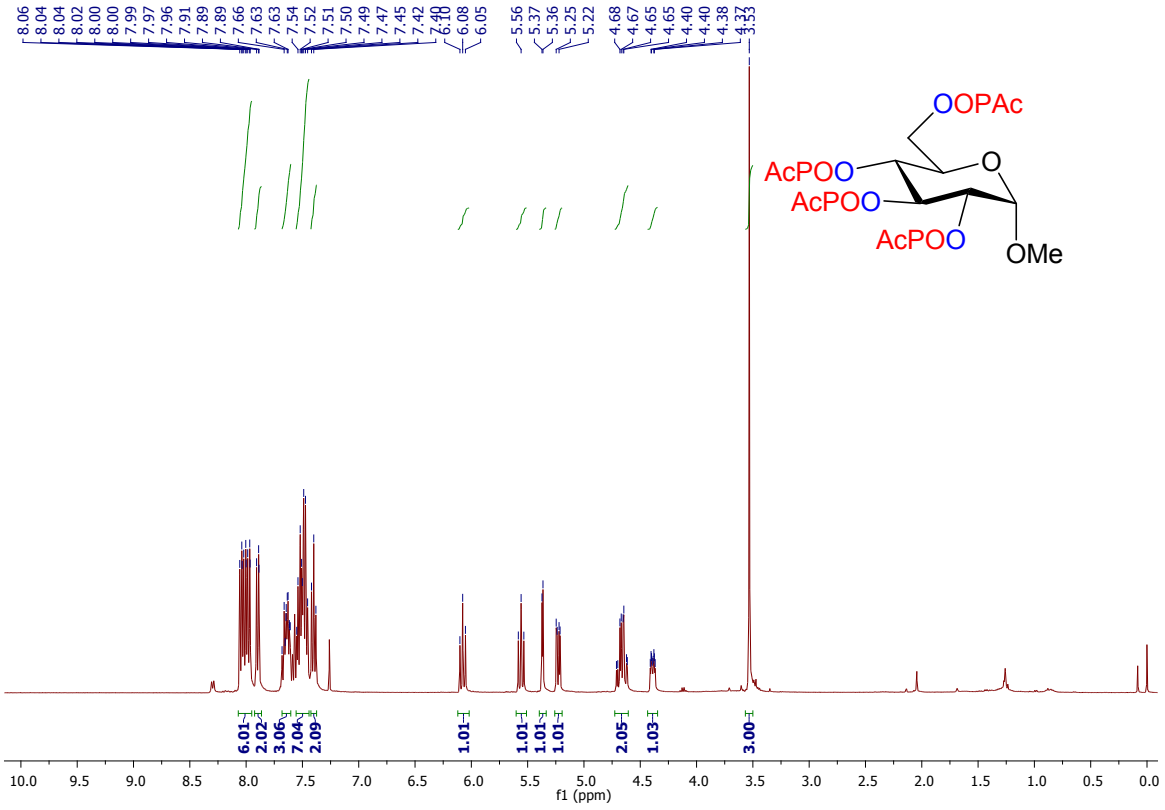
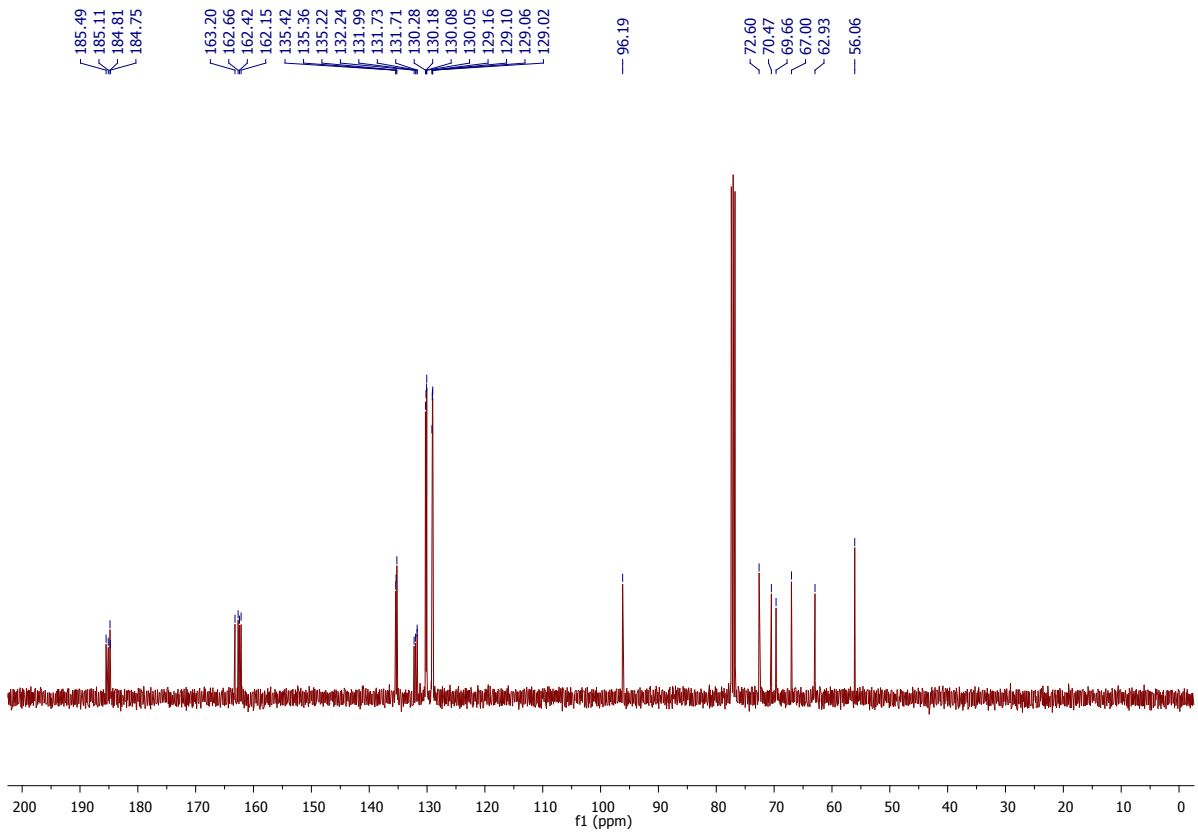




1

H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1d ($CDCl_3$)

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129.16
129.10
129.06
129.02
96.19
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67.00
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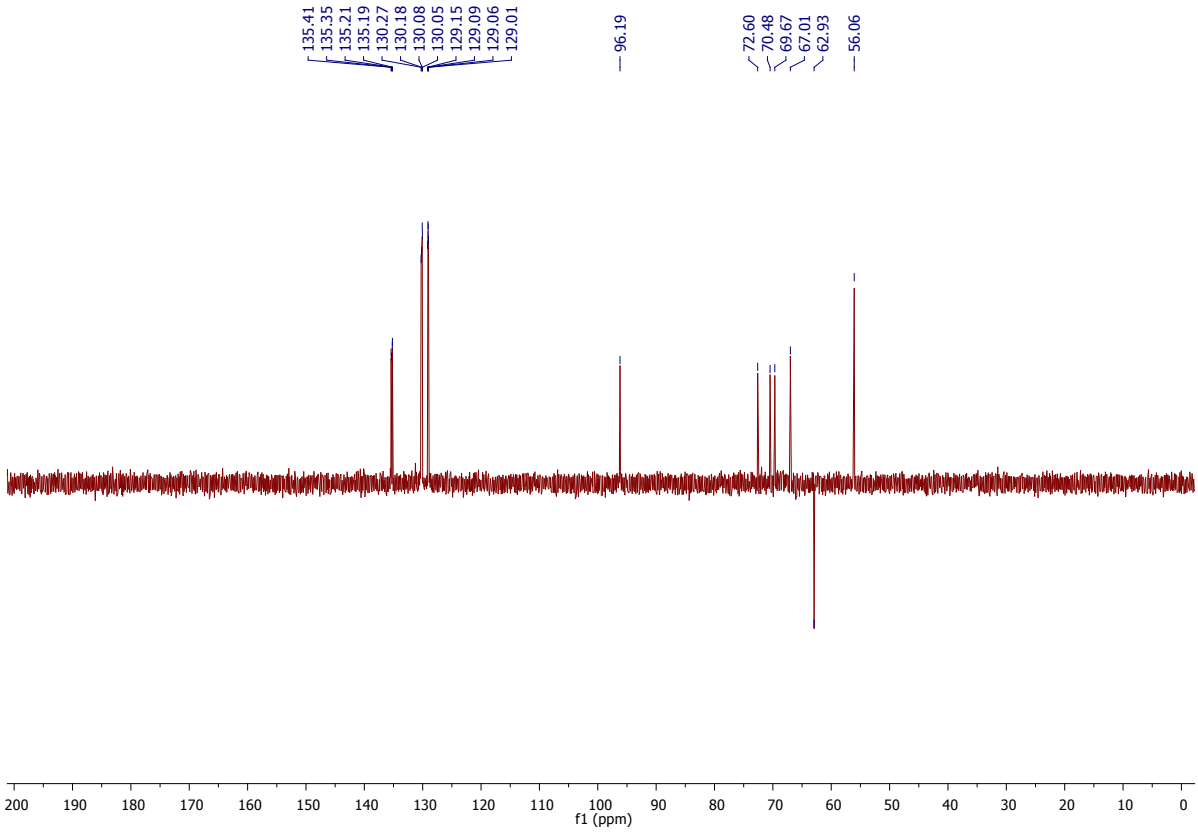
f1 (ppm)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67.01
62.93
56.06
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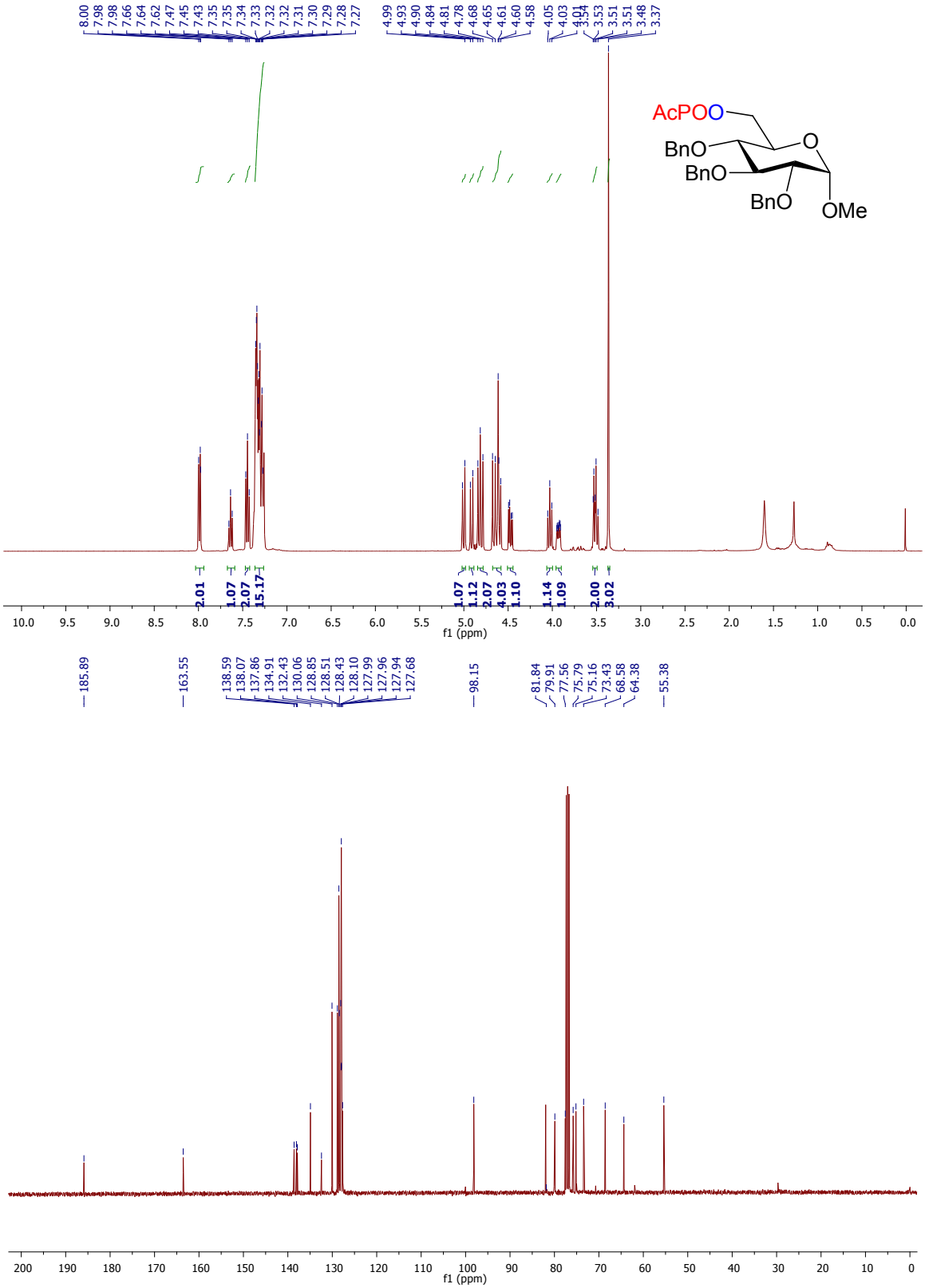
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1e ($CDCl_3$)



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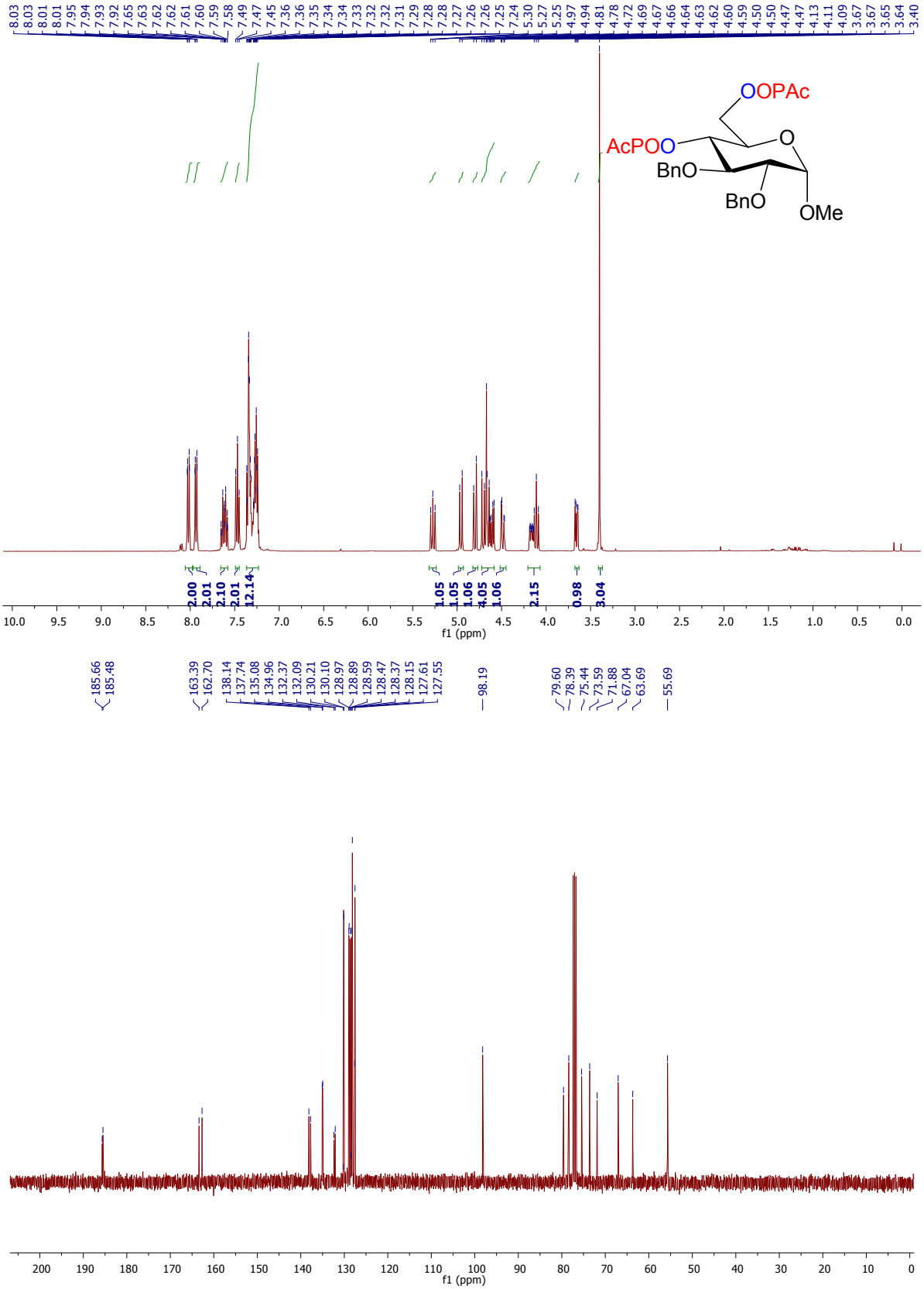

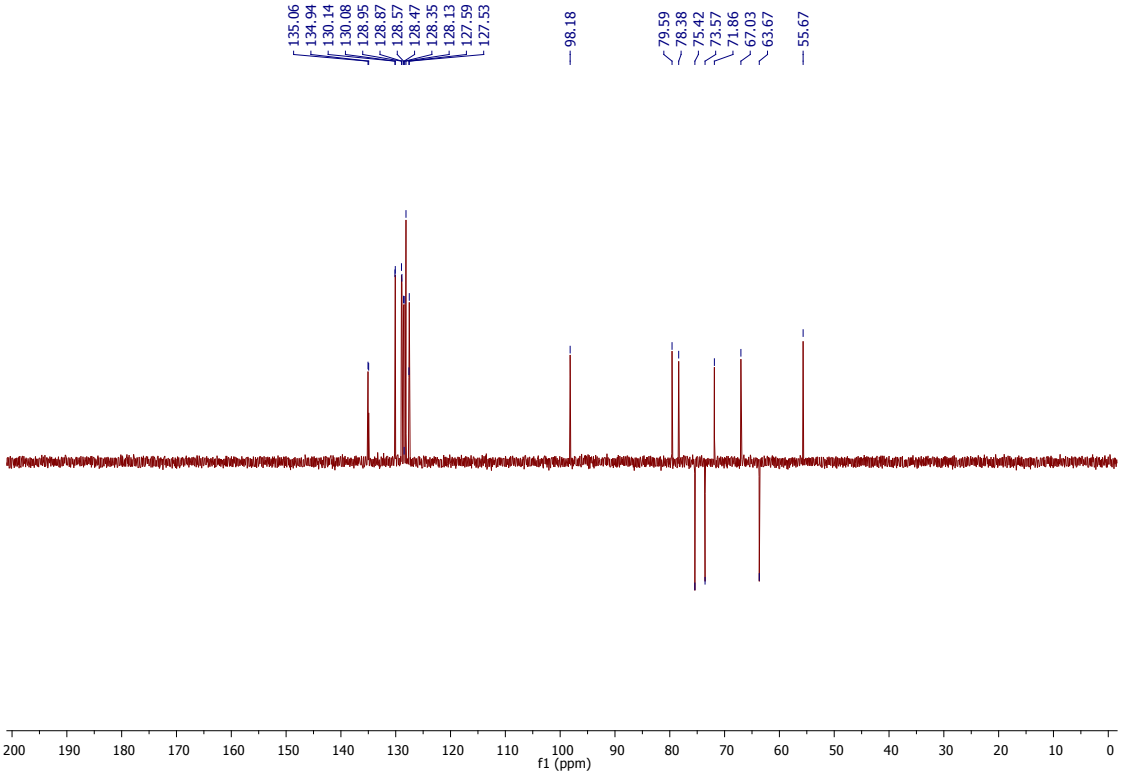

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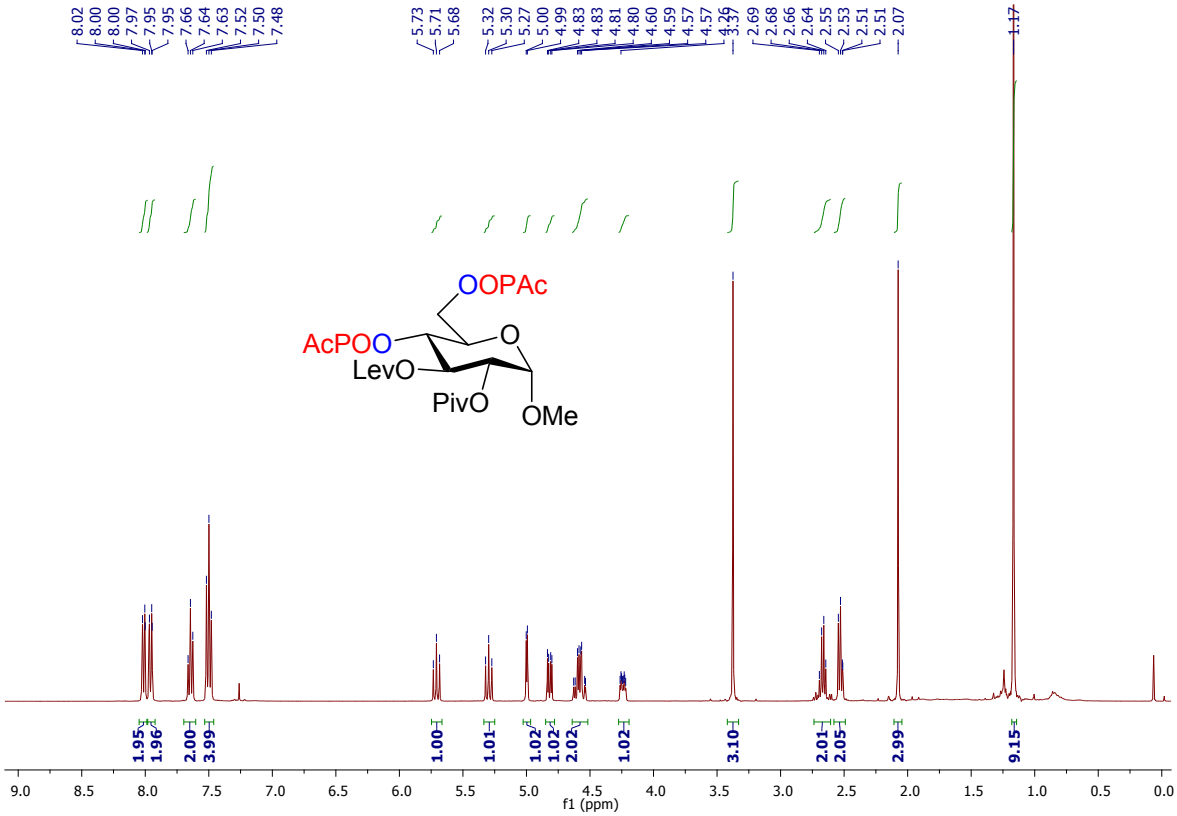

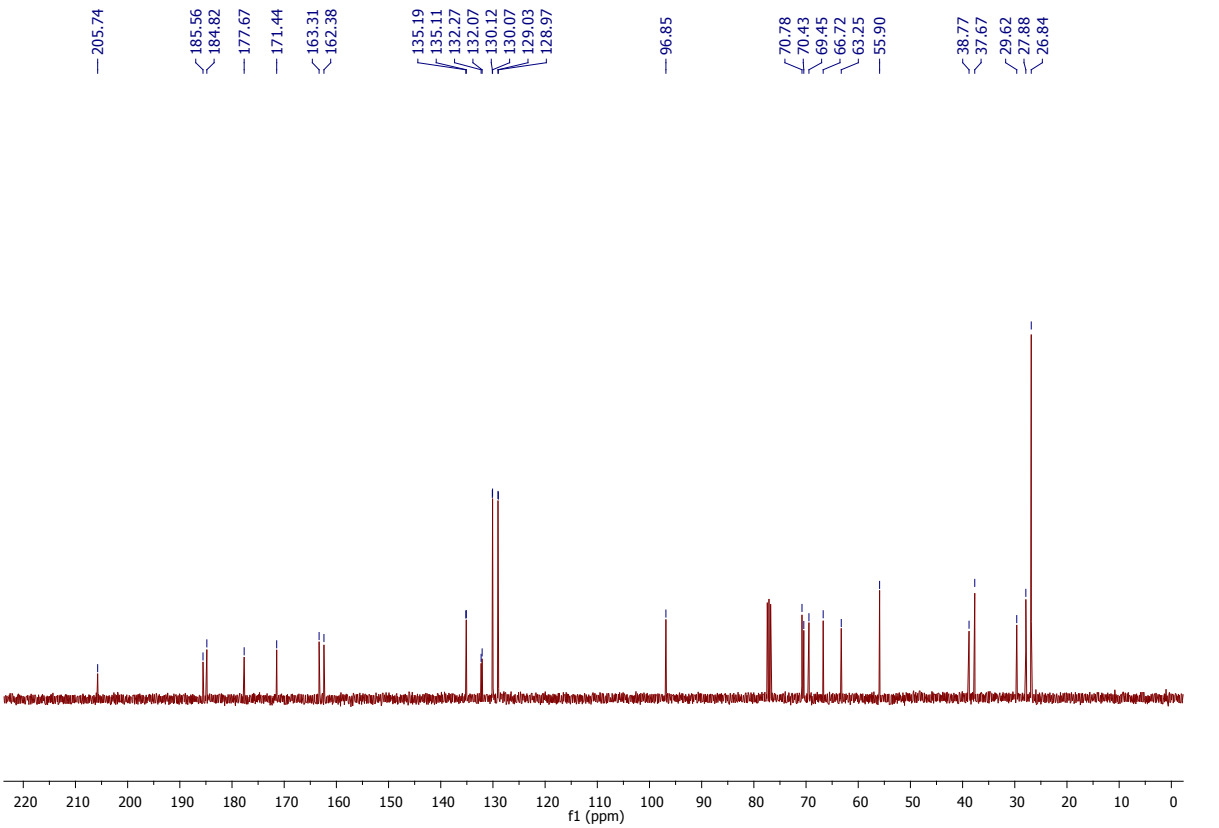
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130.07
129.03
128.97
96.85
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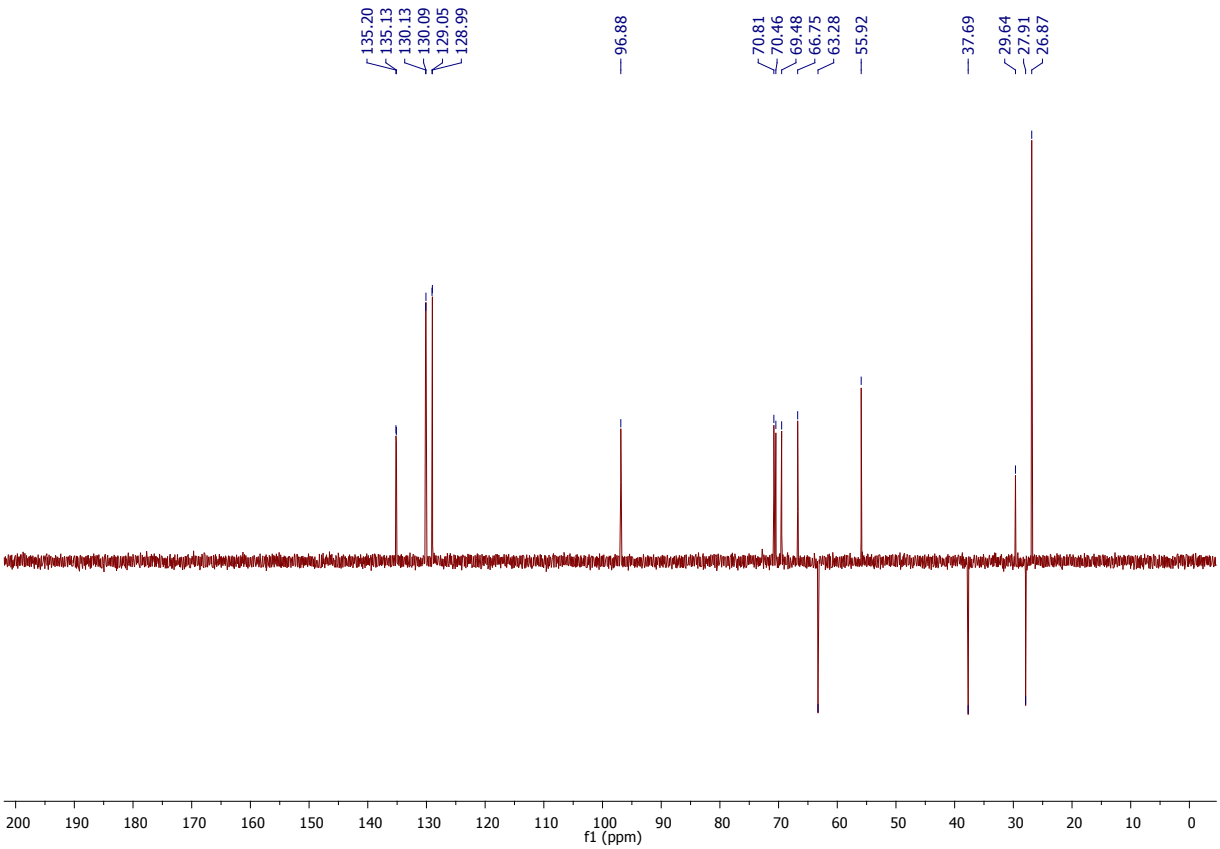
f1 (ppm)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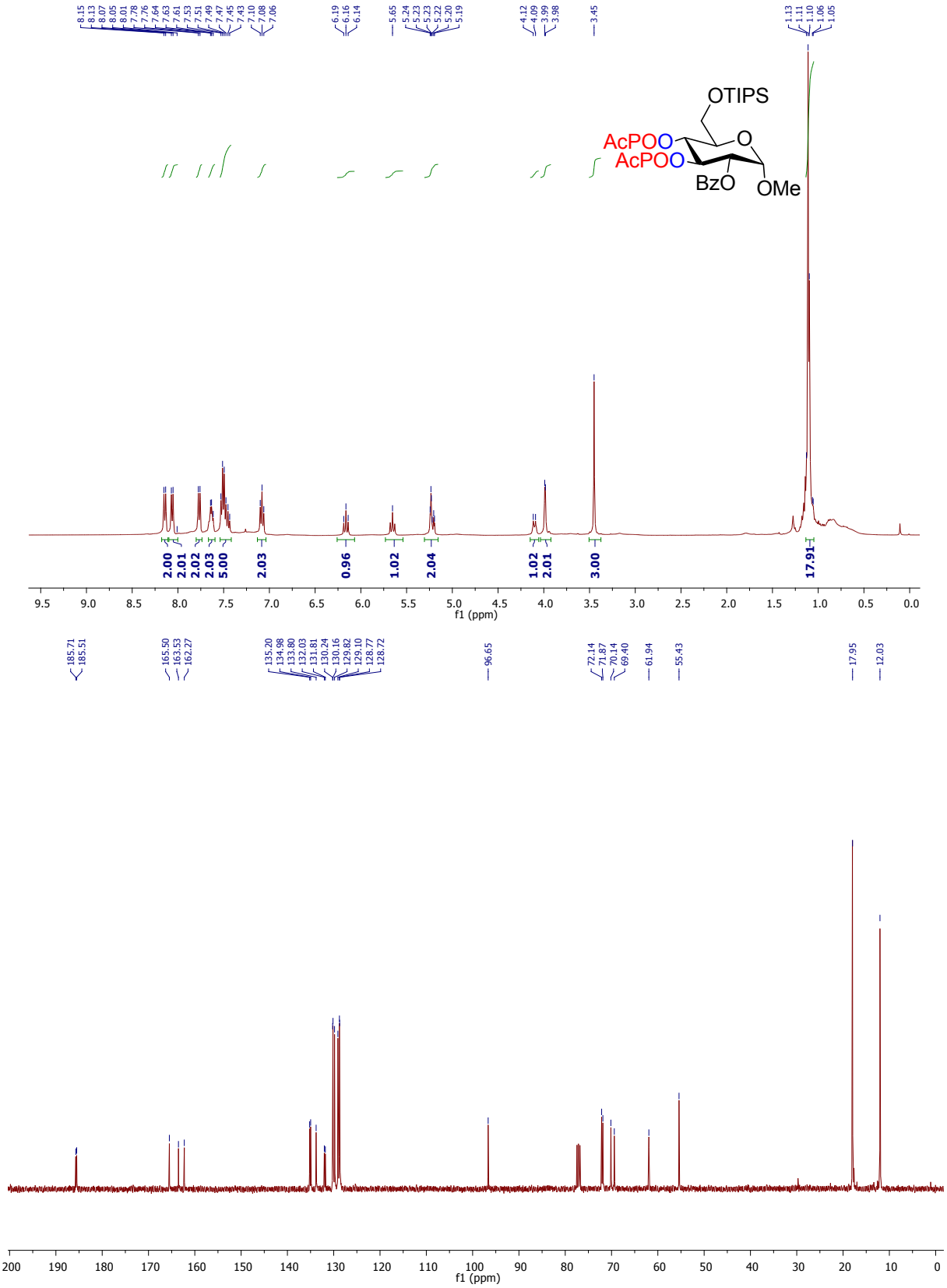
f1 (ppm)

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1h ($CDCl_3$)



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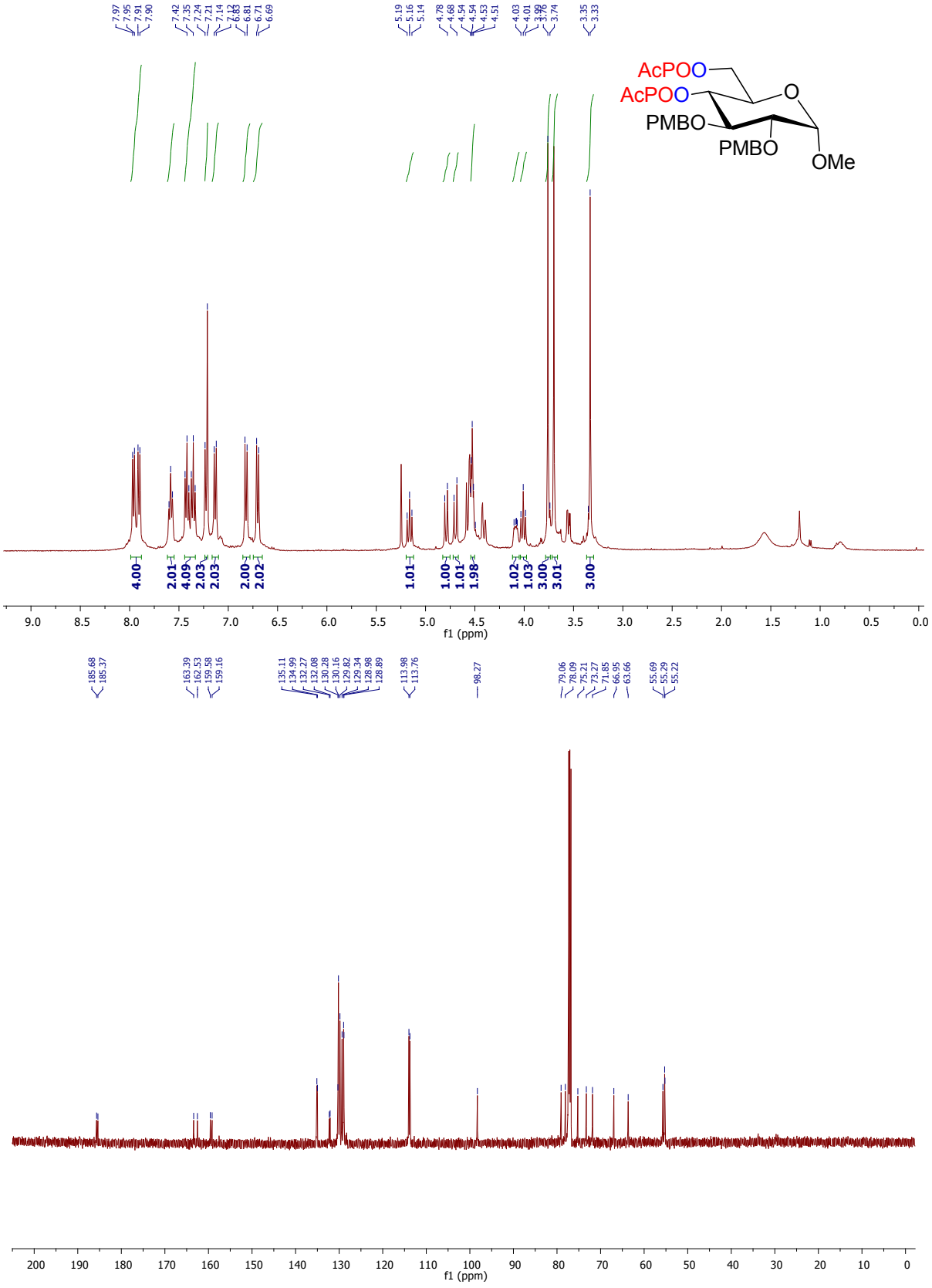

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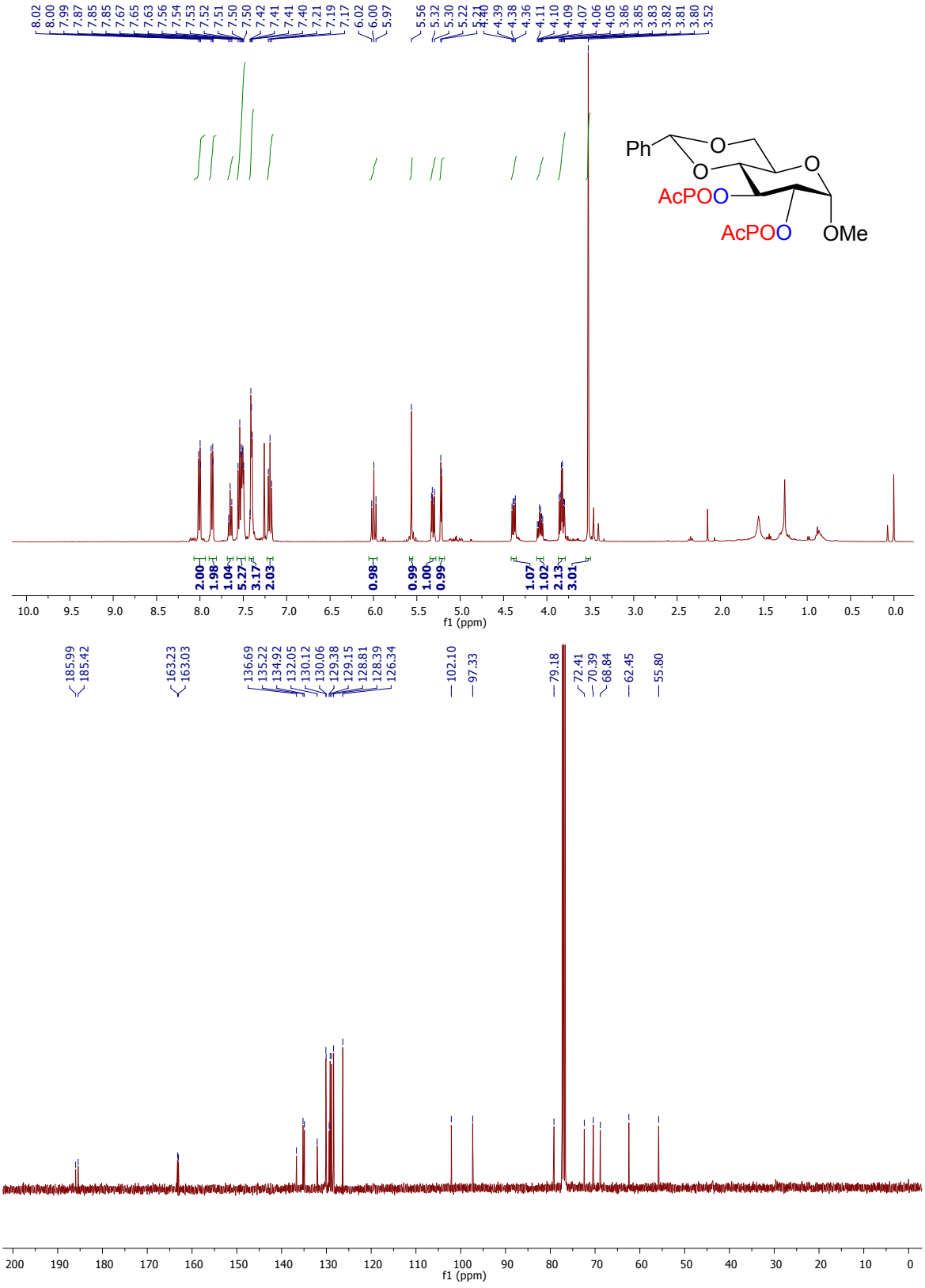

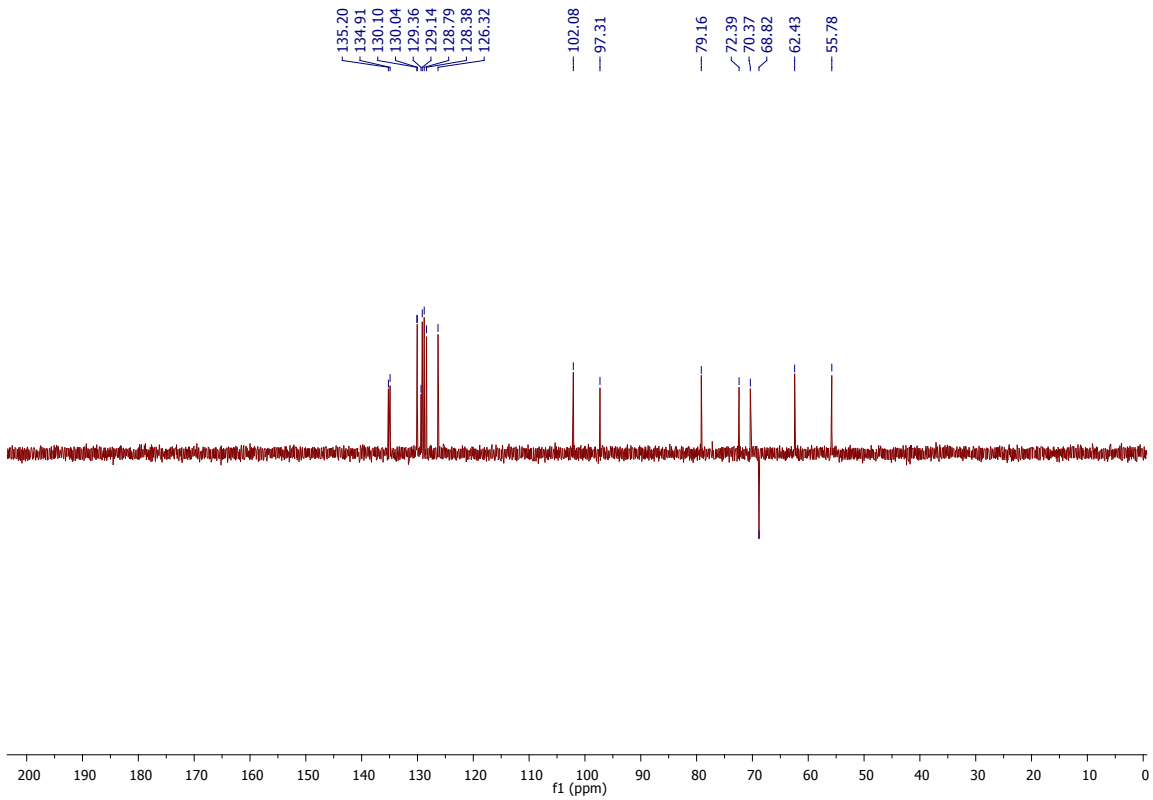

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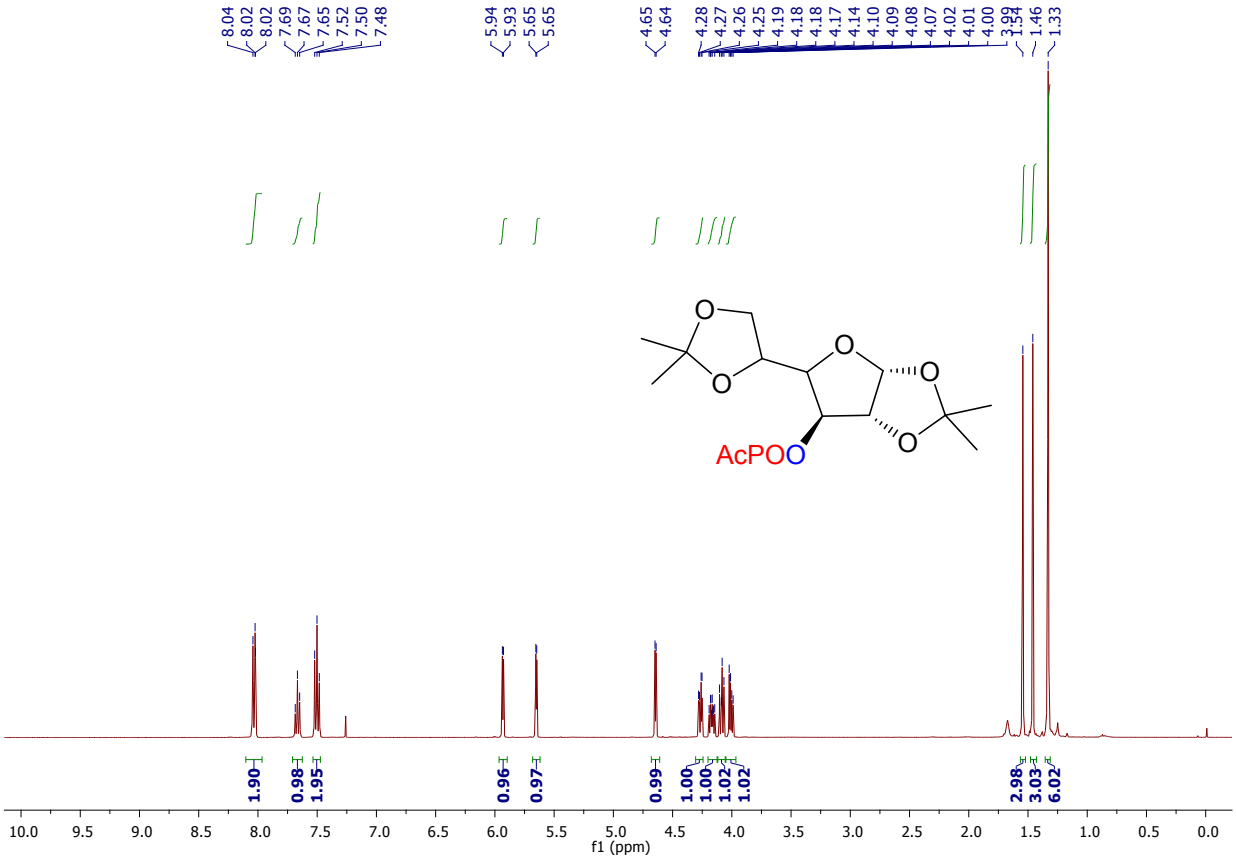

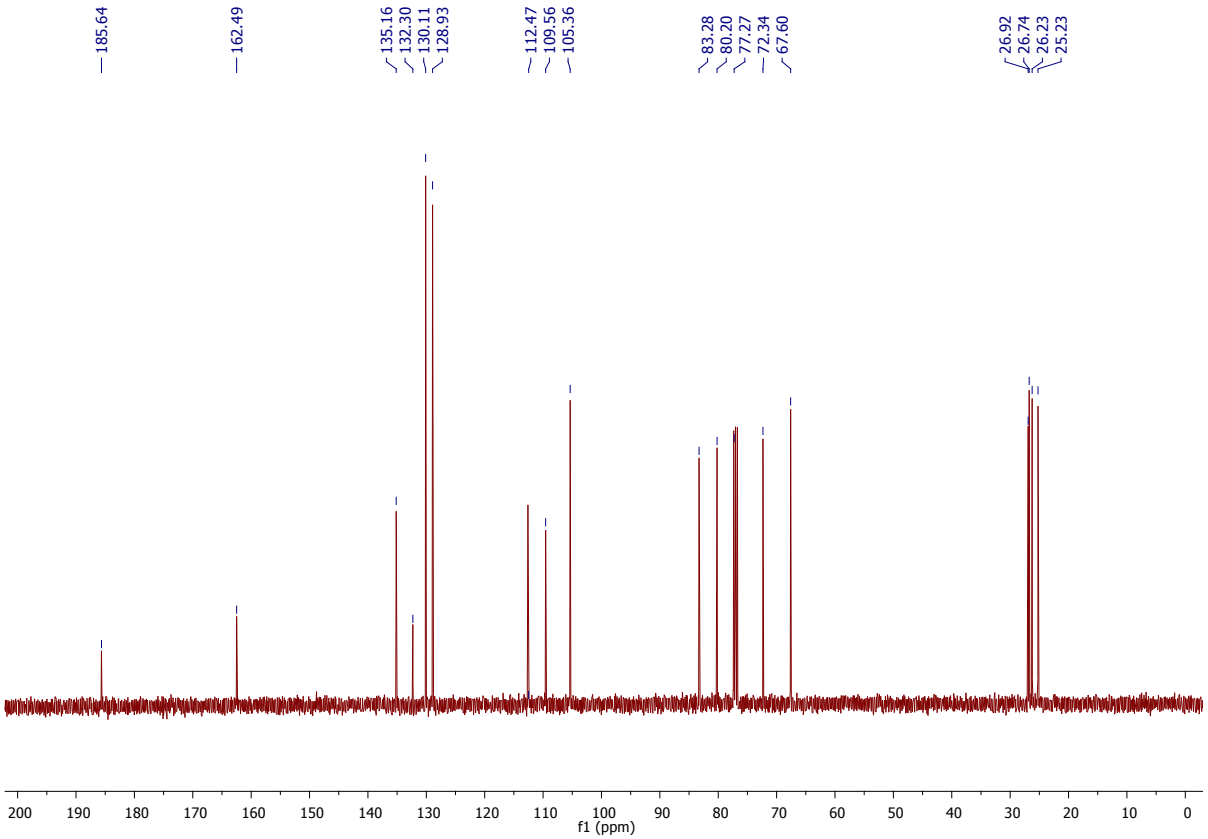
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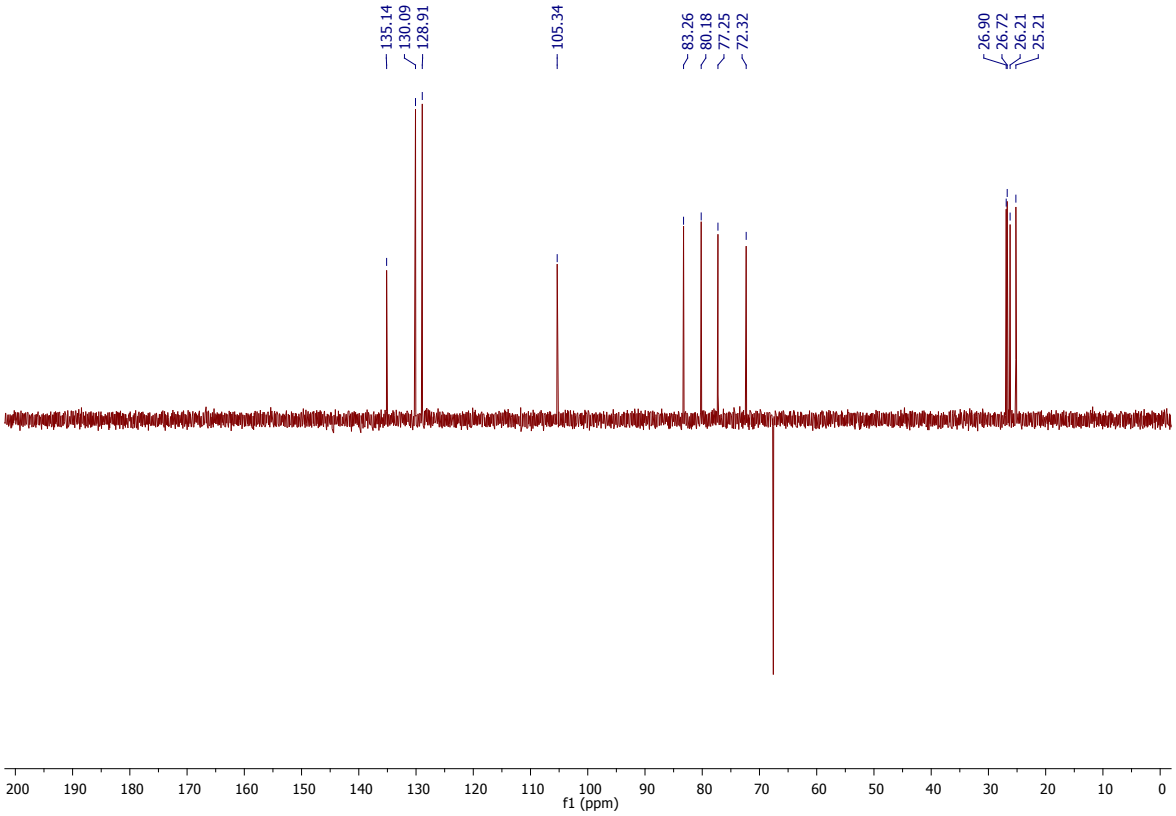
f1 (ppm)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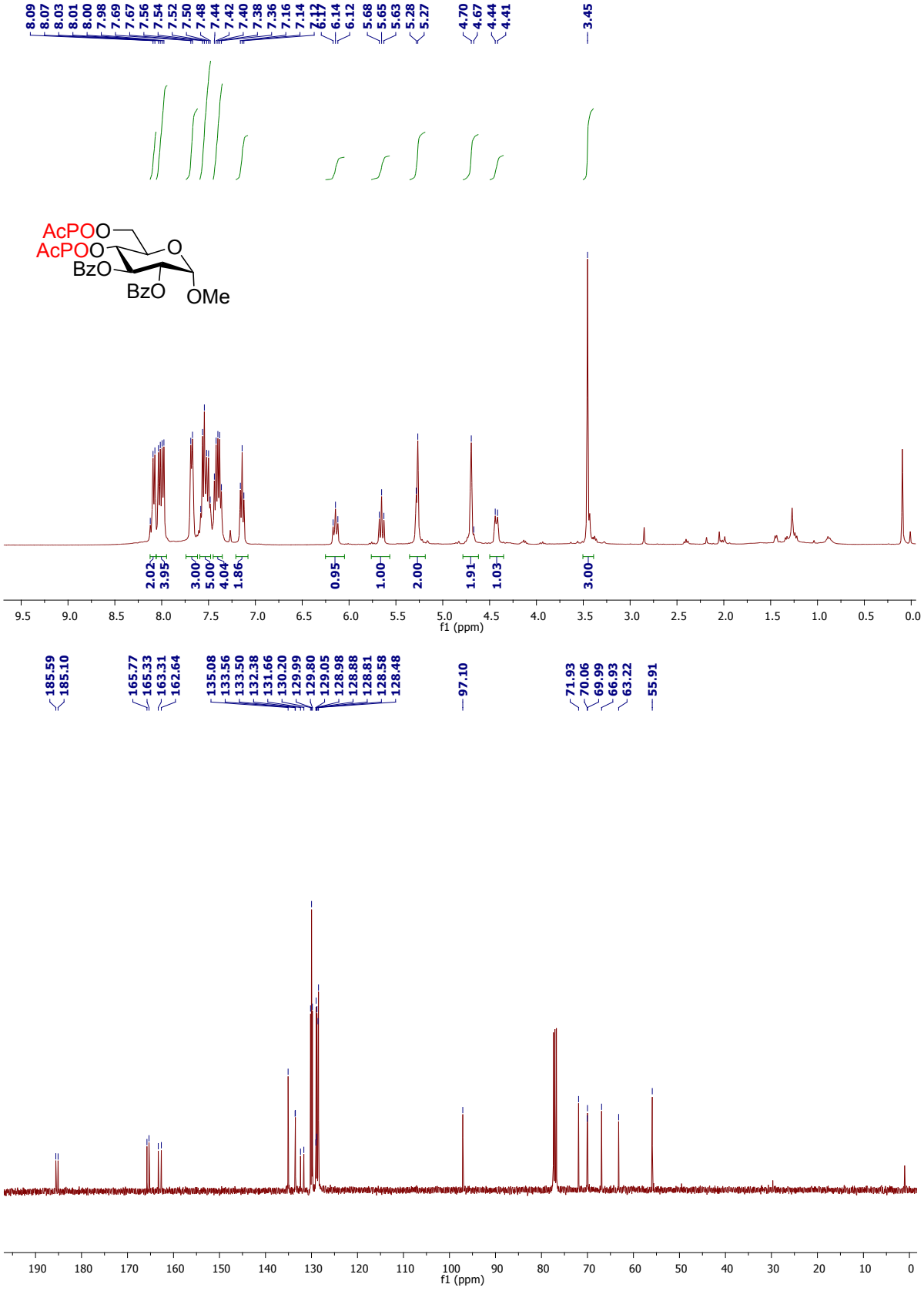
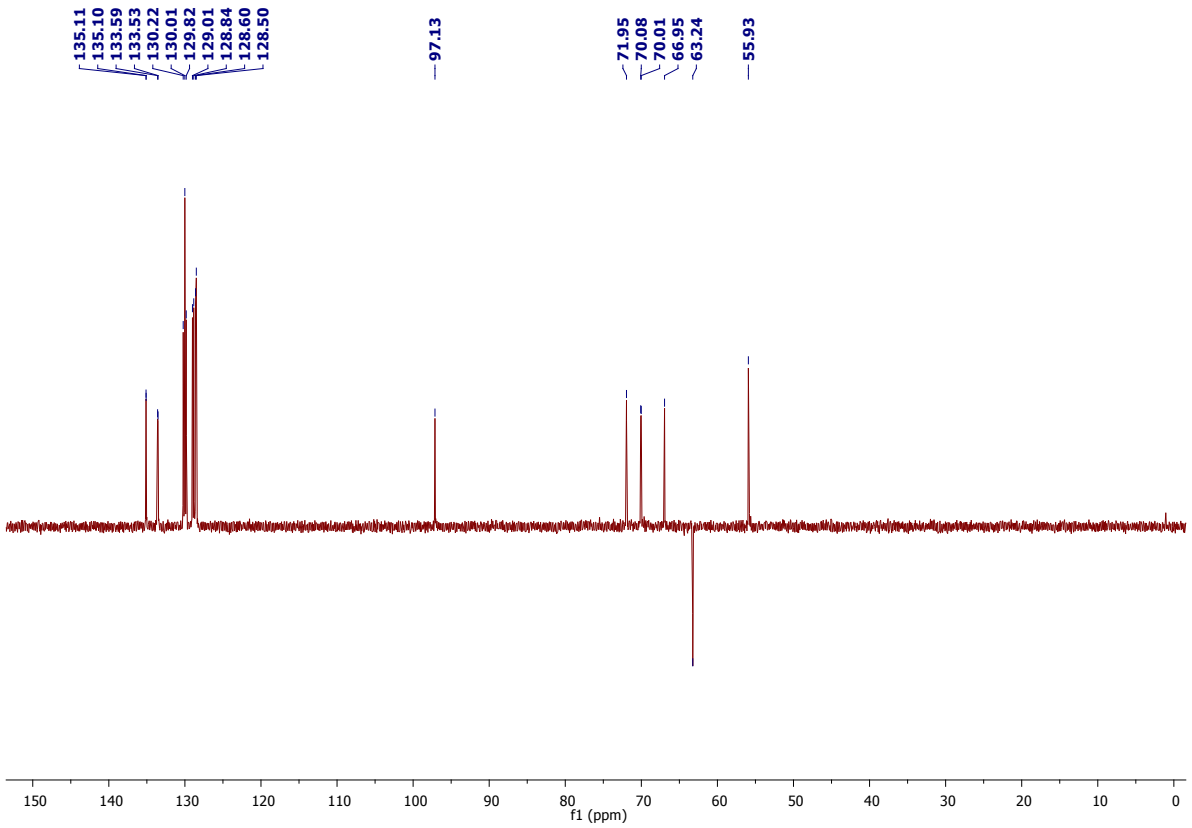
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 1l ($CDCl_3$)





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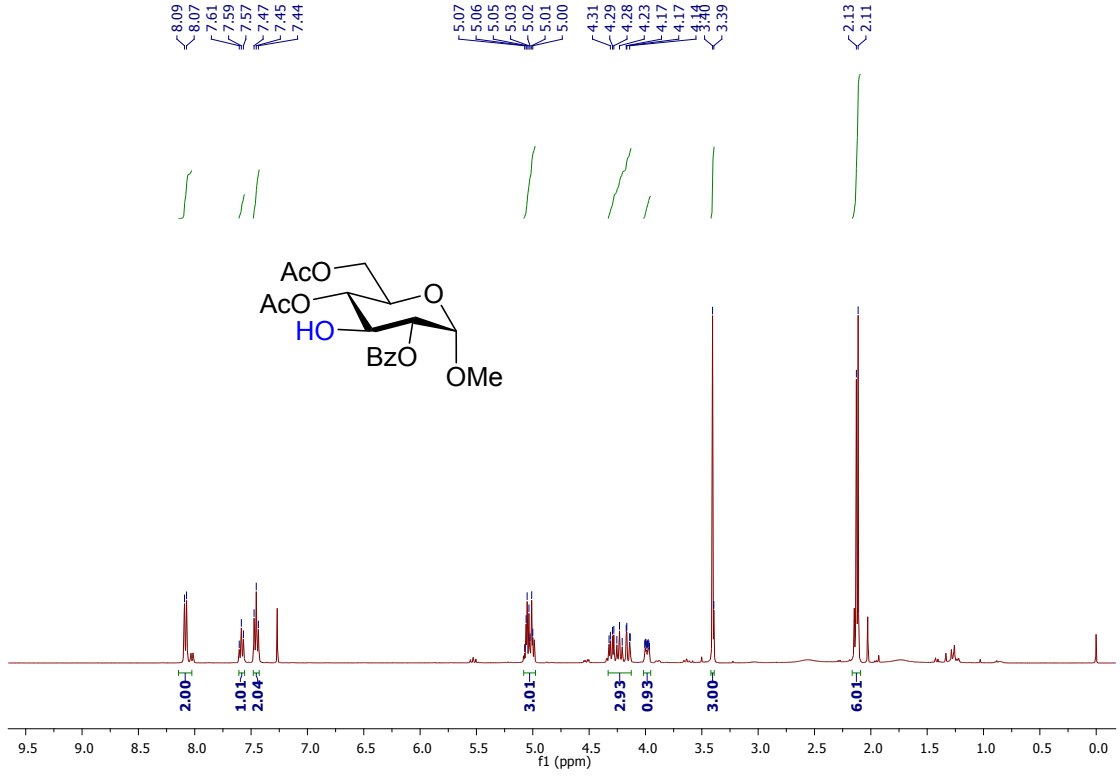

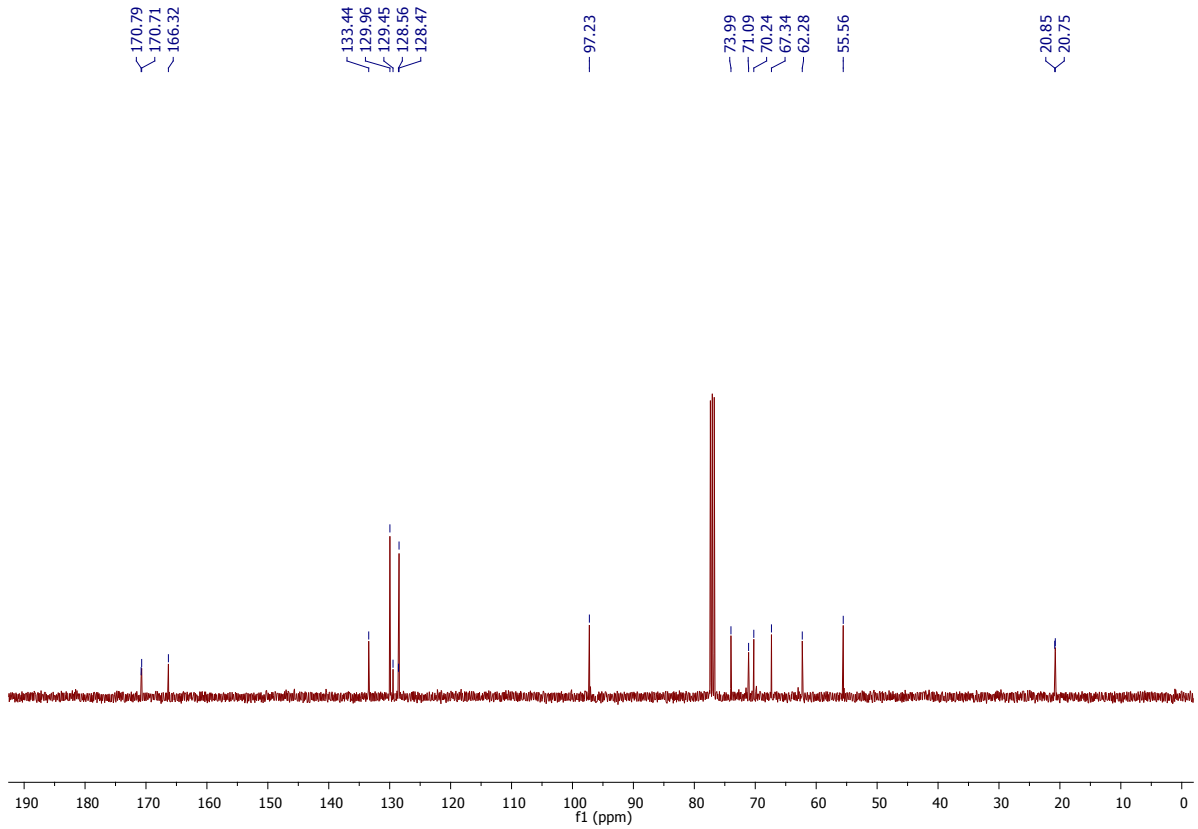
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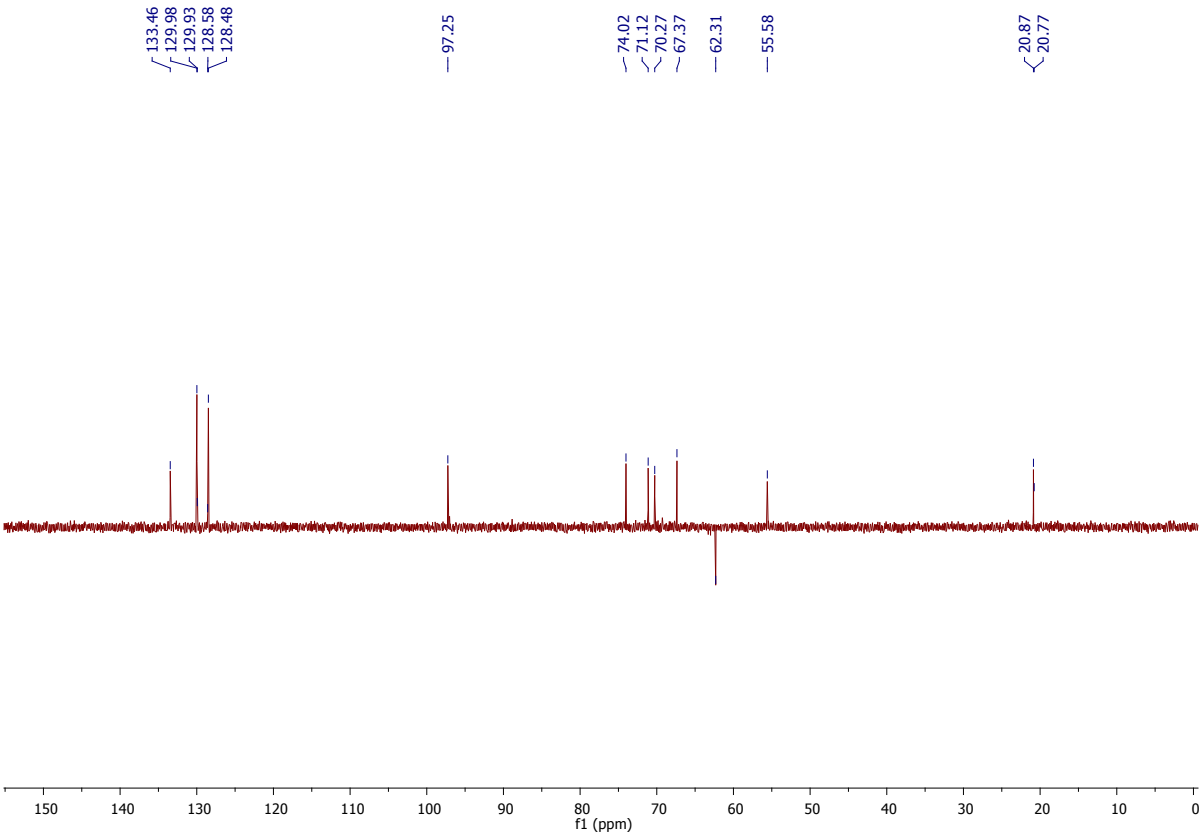
f1 (ppm)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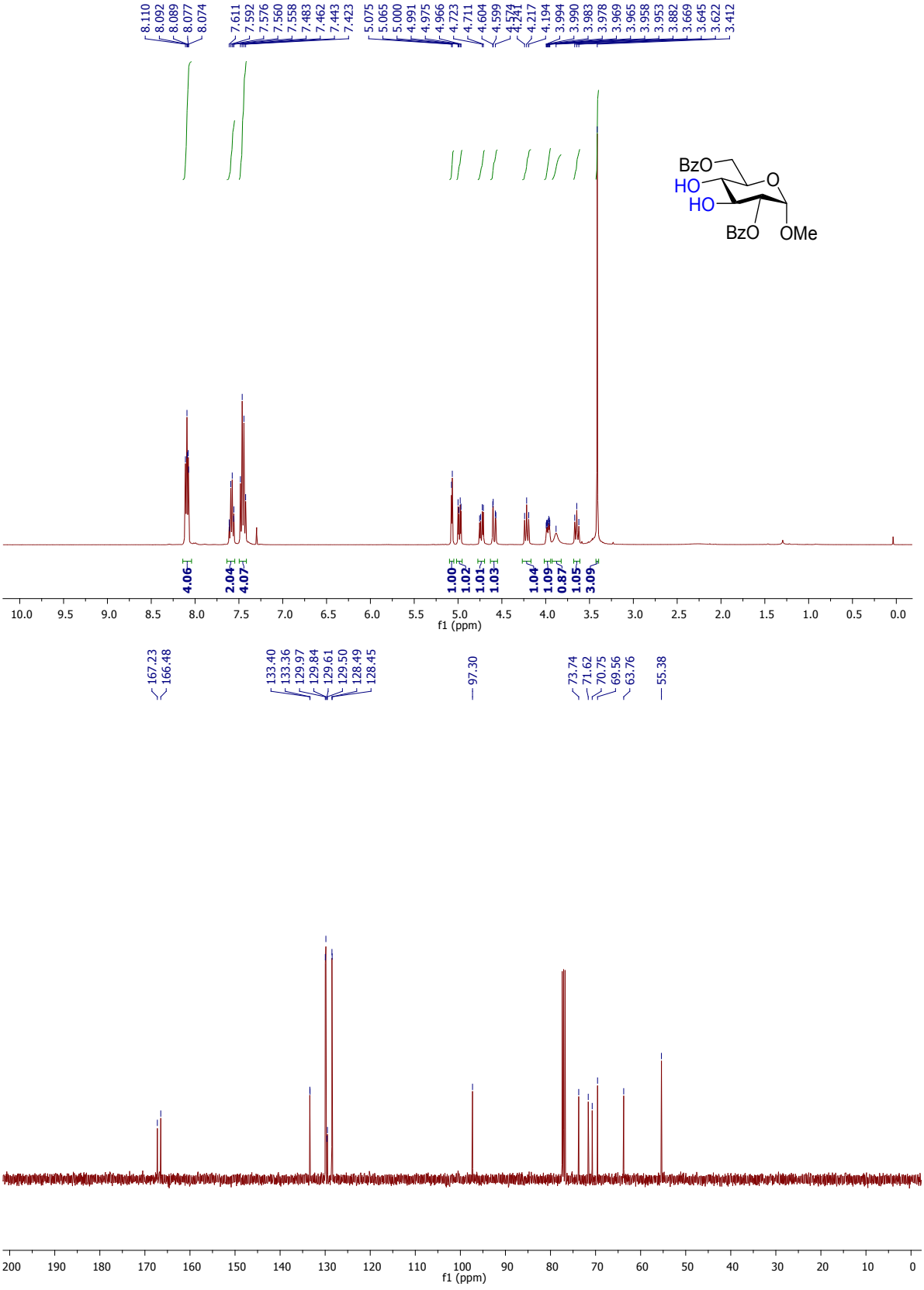

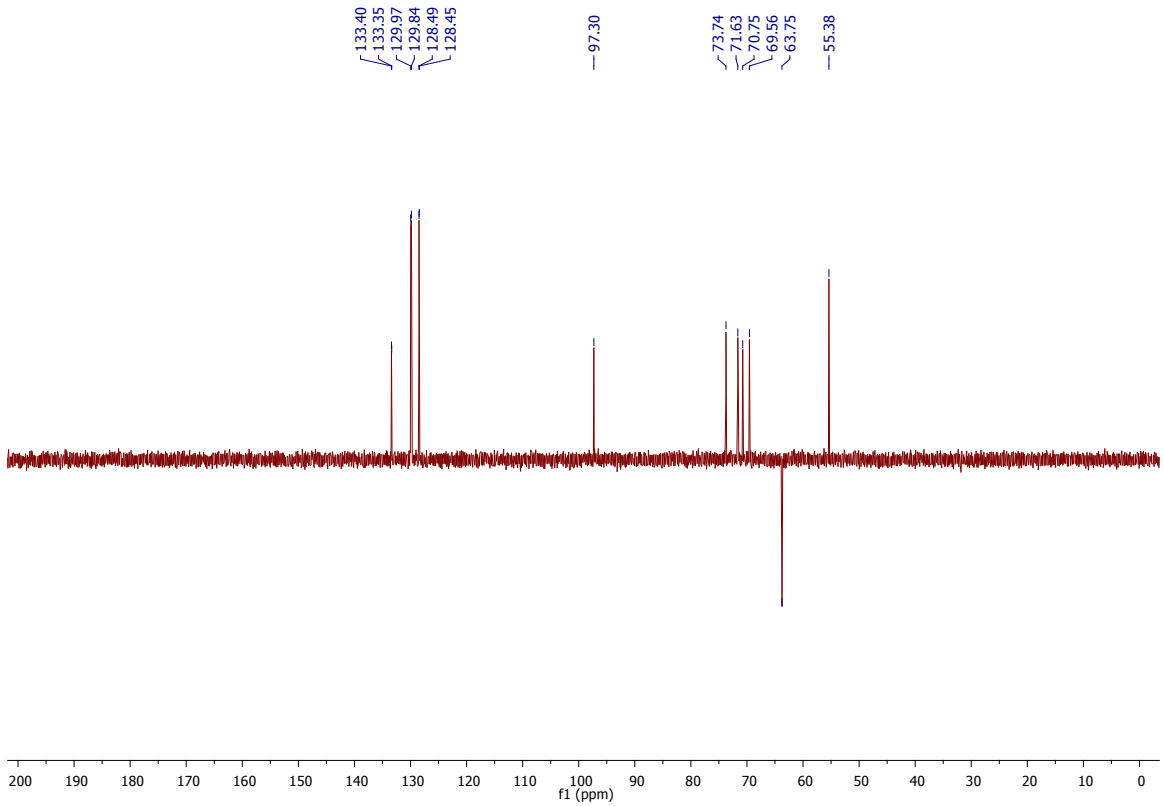

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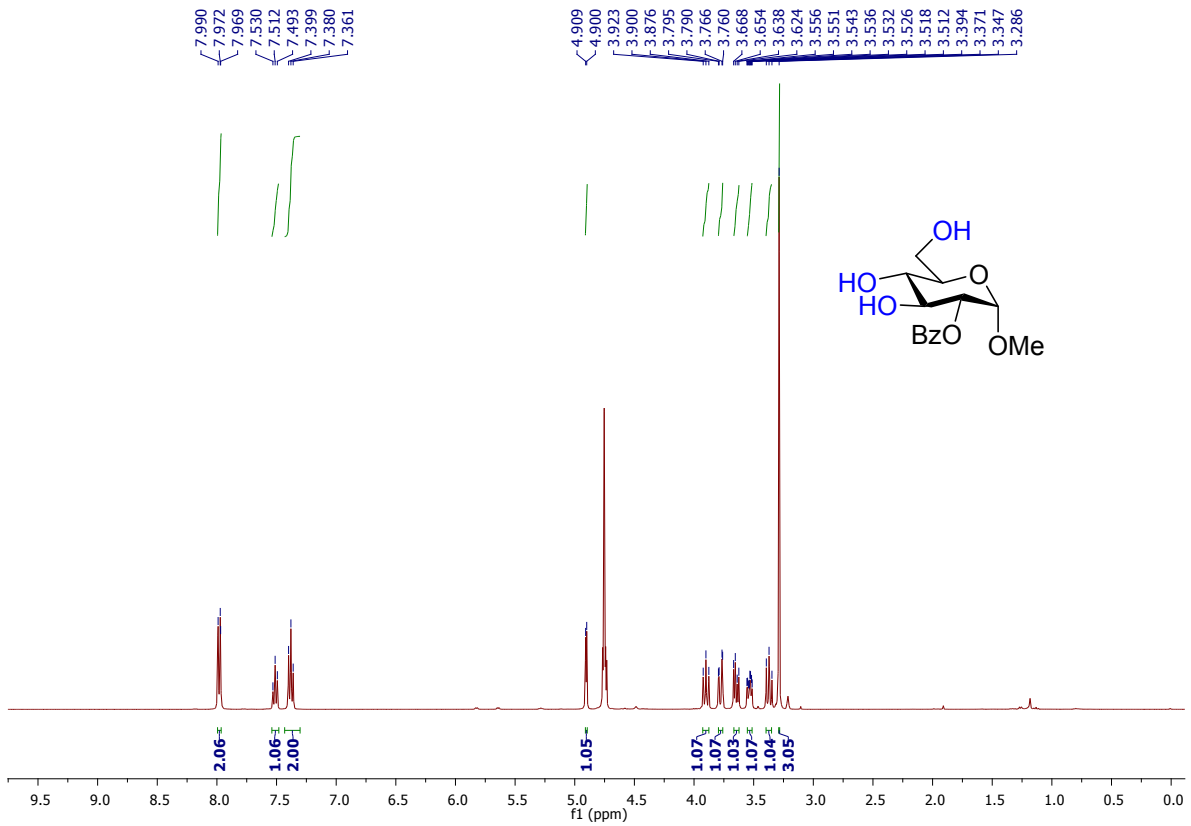

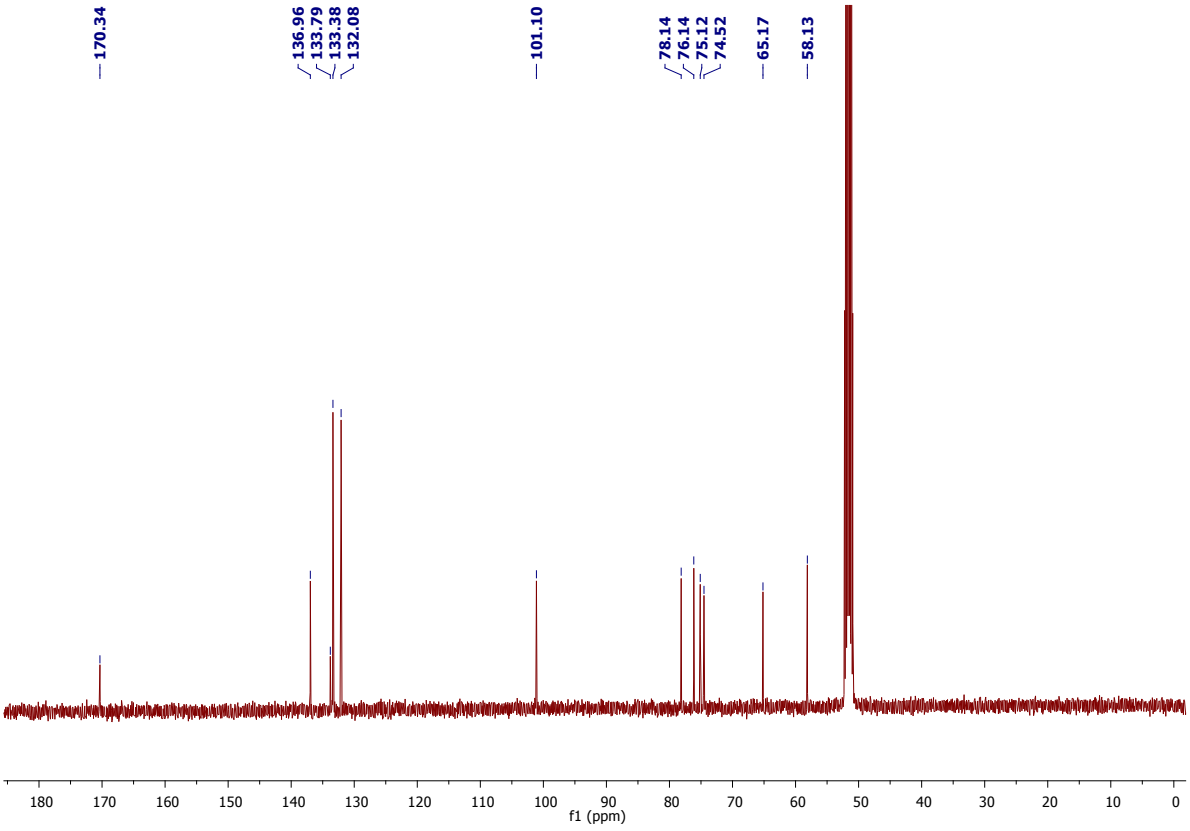
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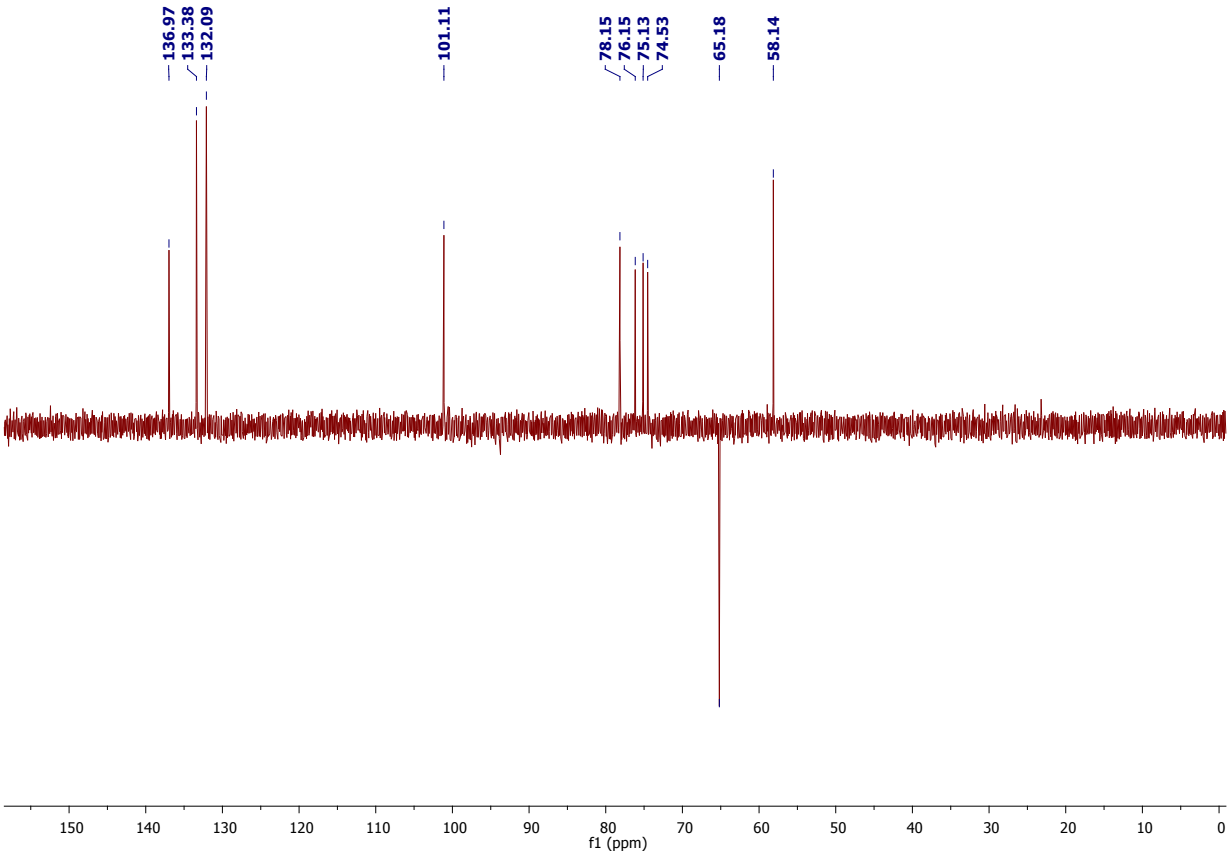
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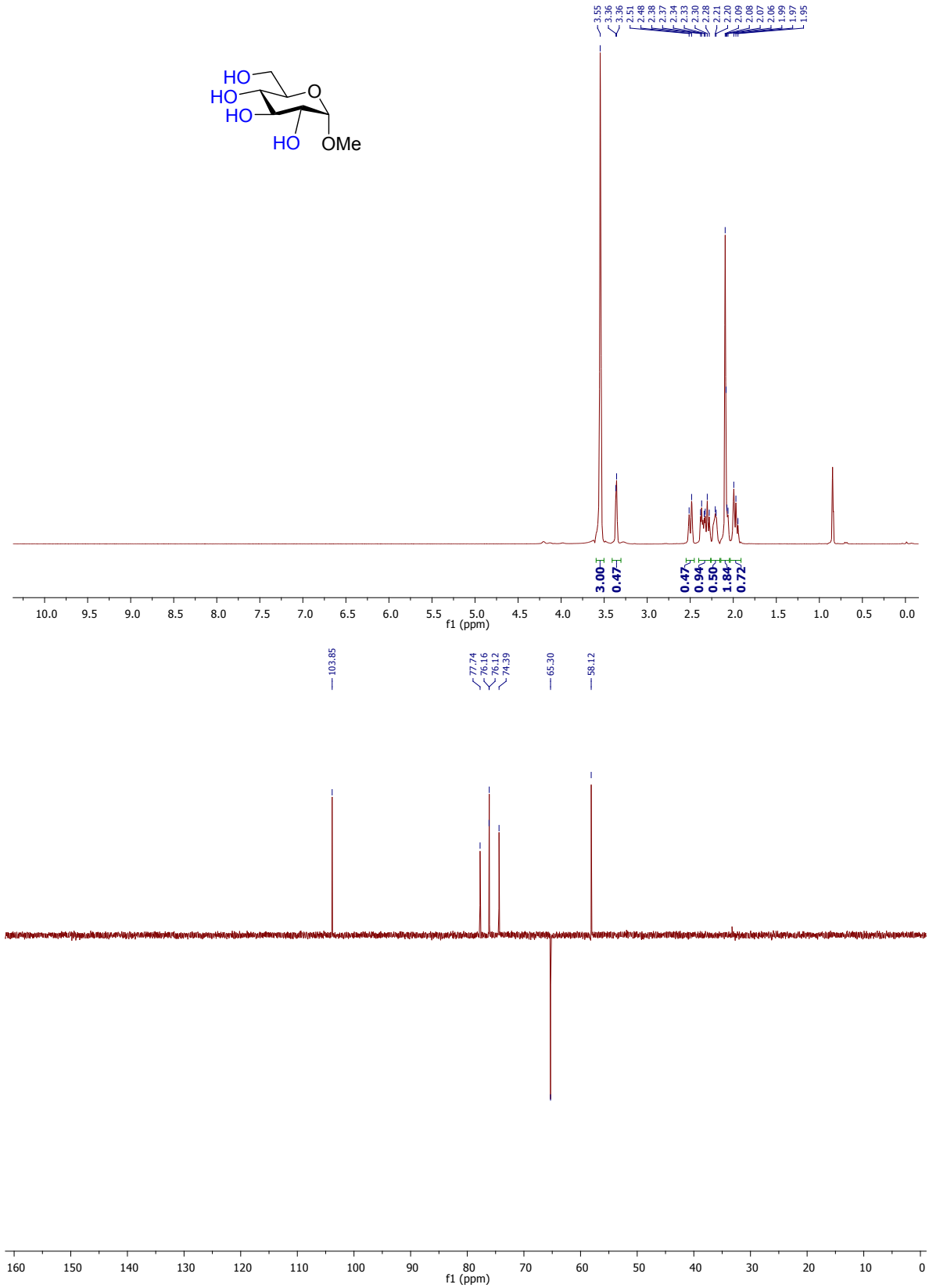
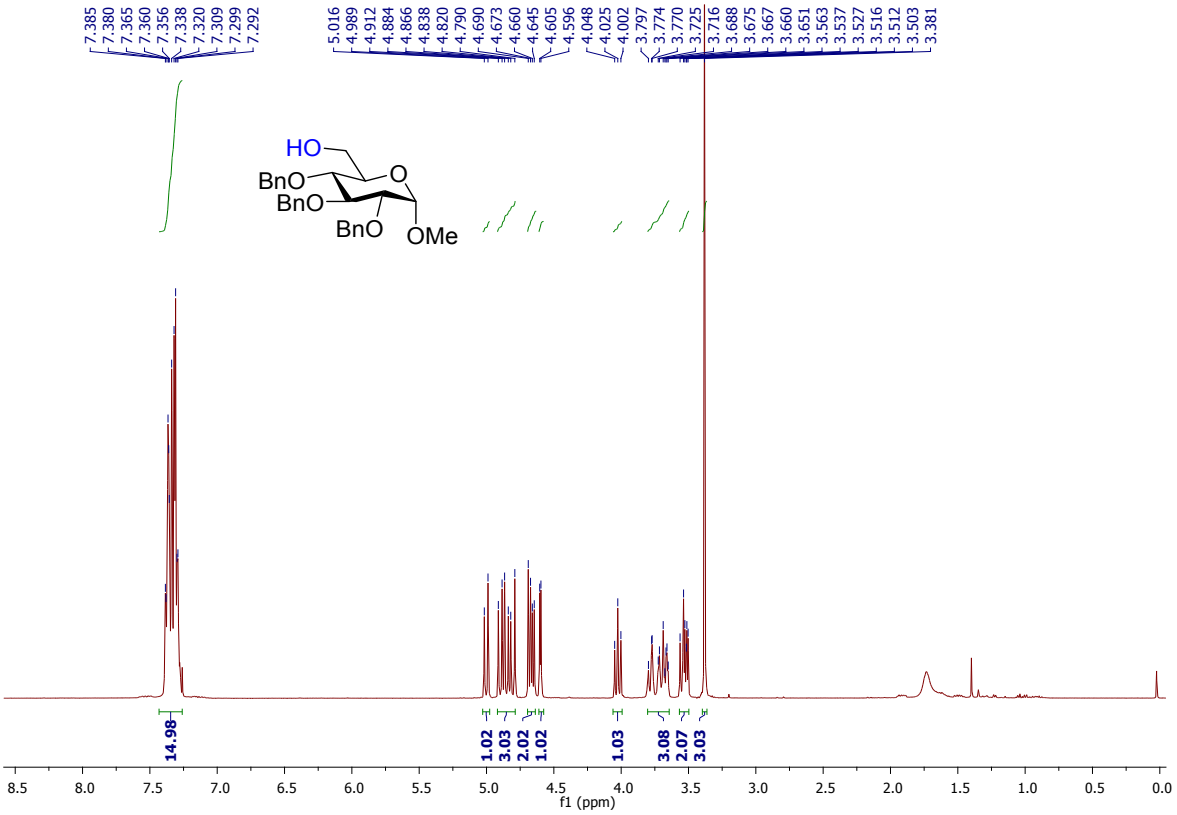
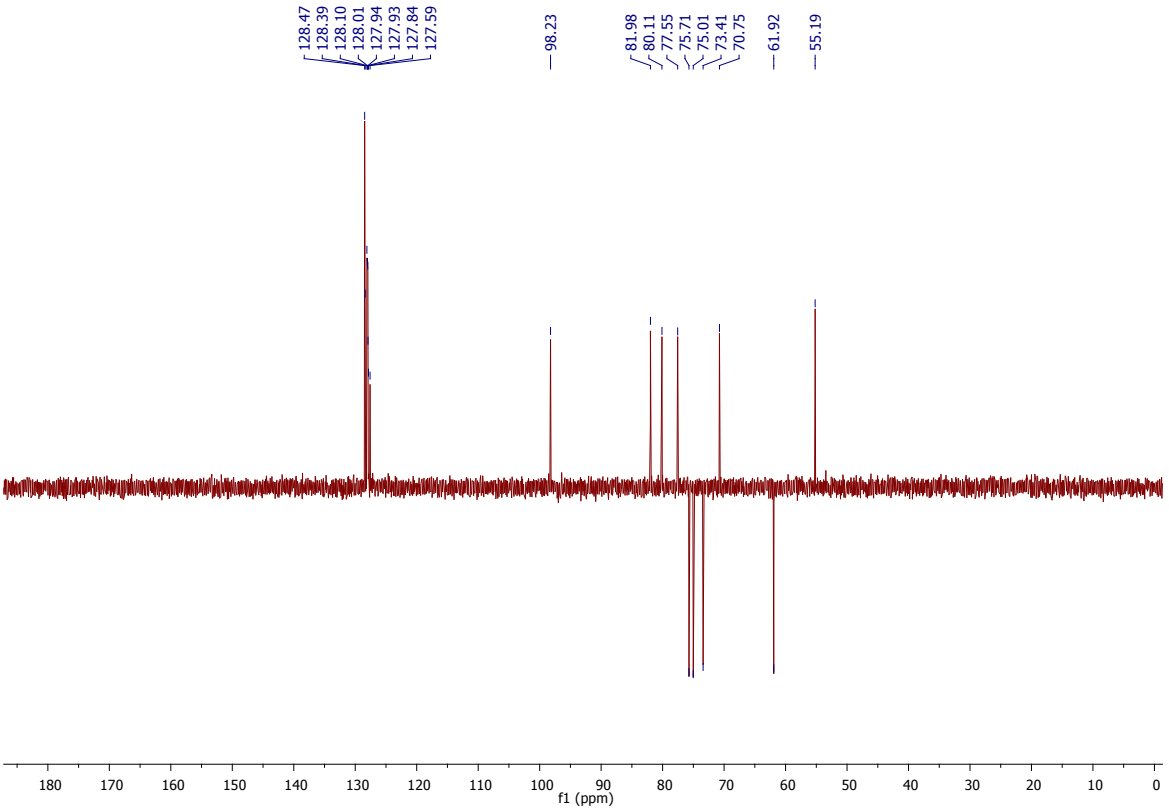
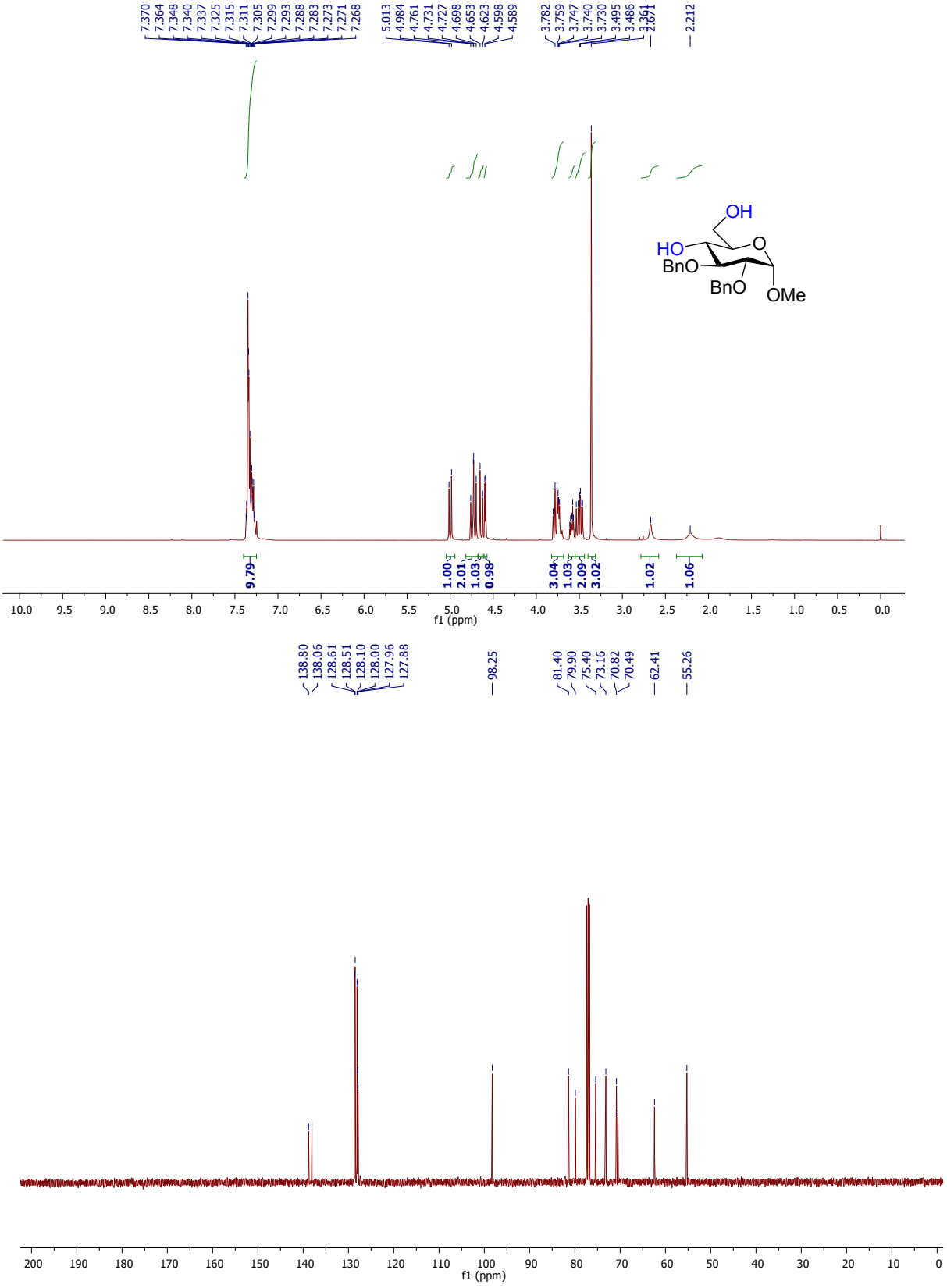


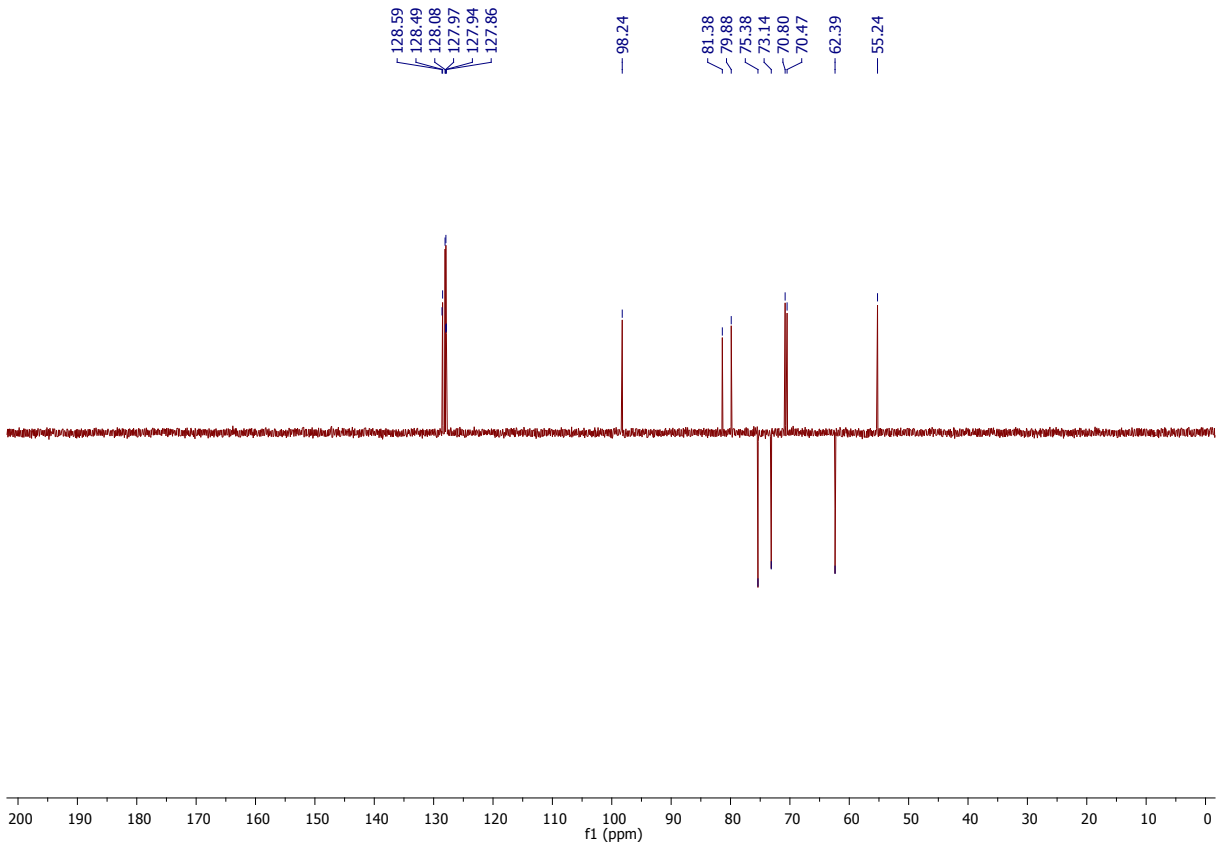
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2e ($CDCl_3$)



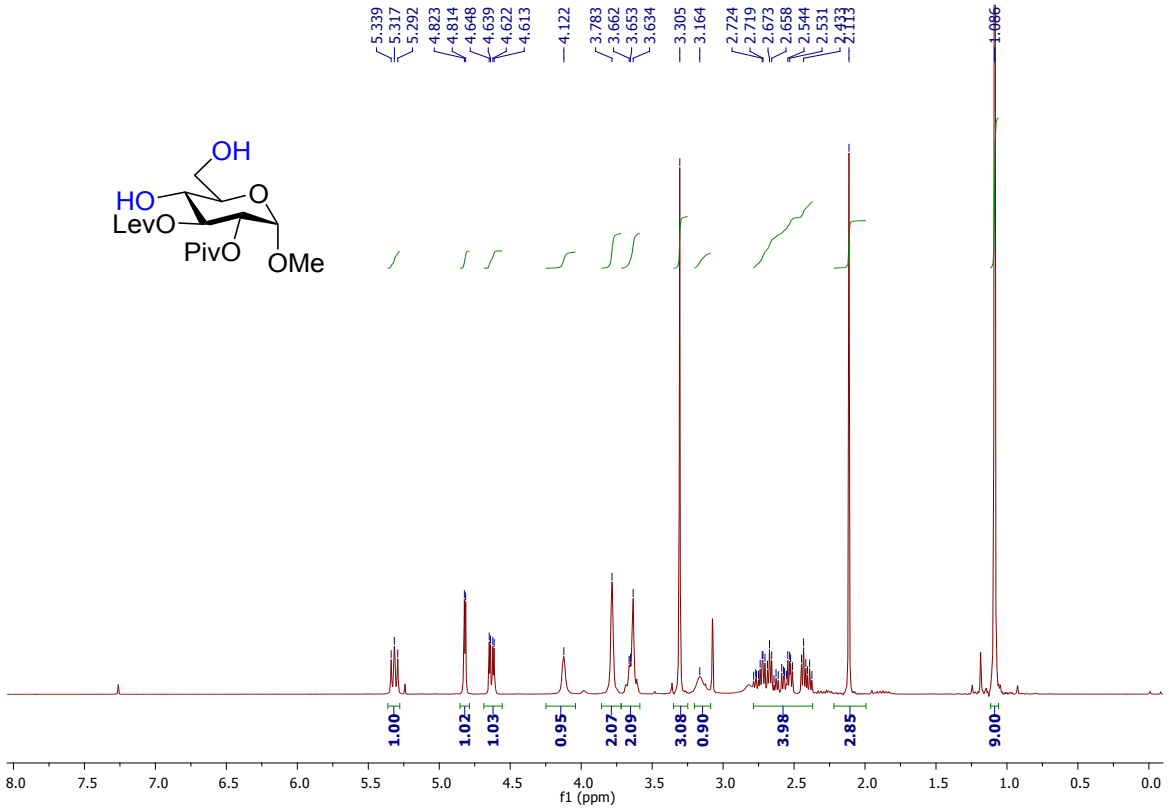


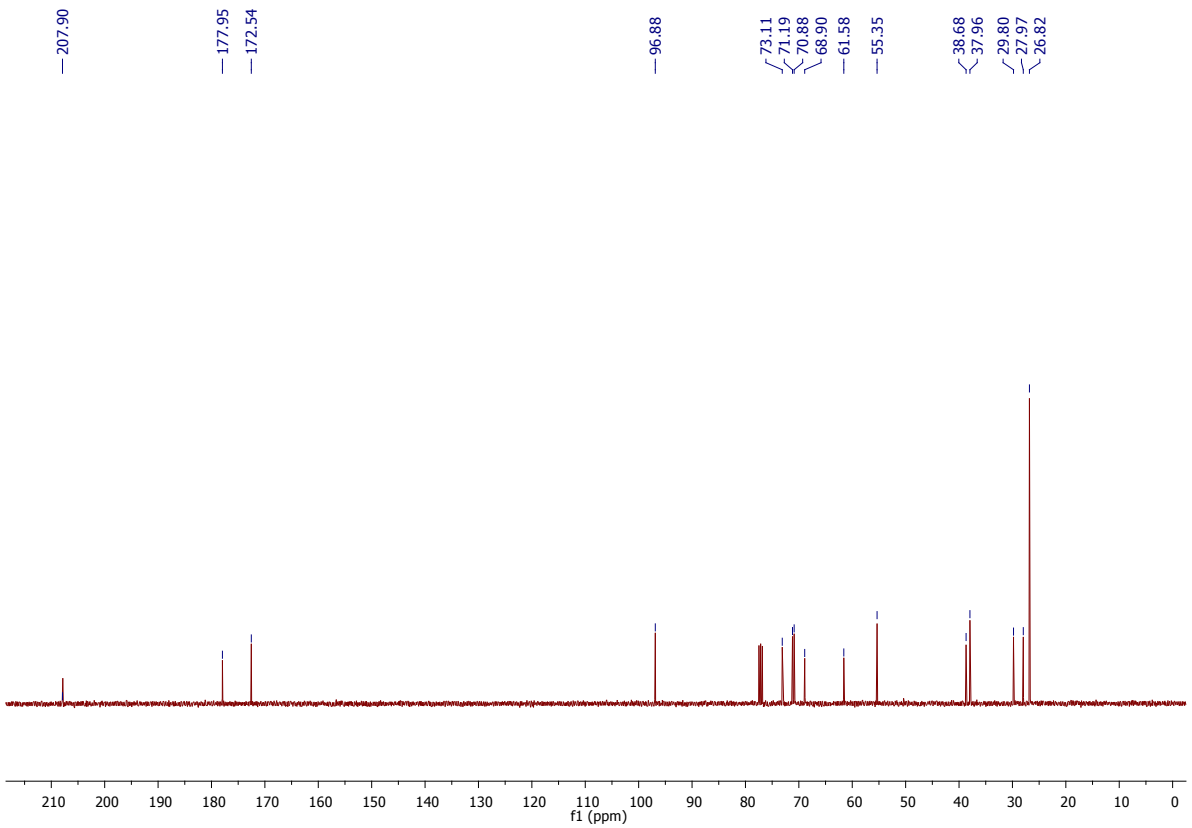
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2f ($CDCl_3$)

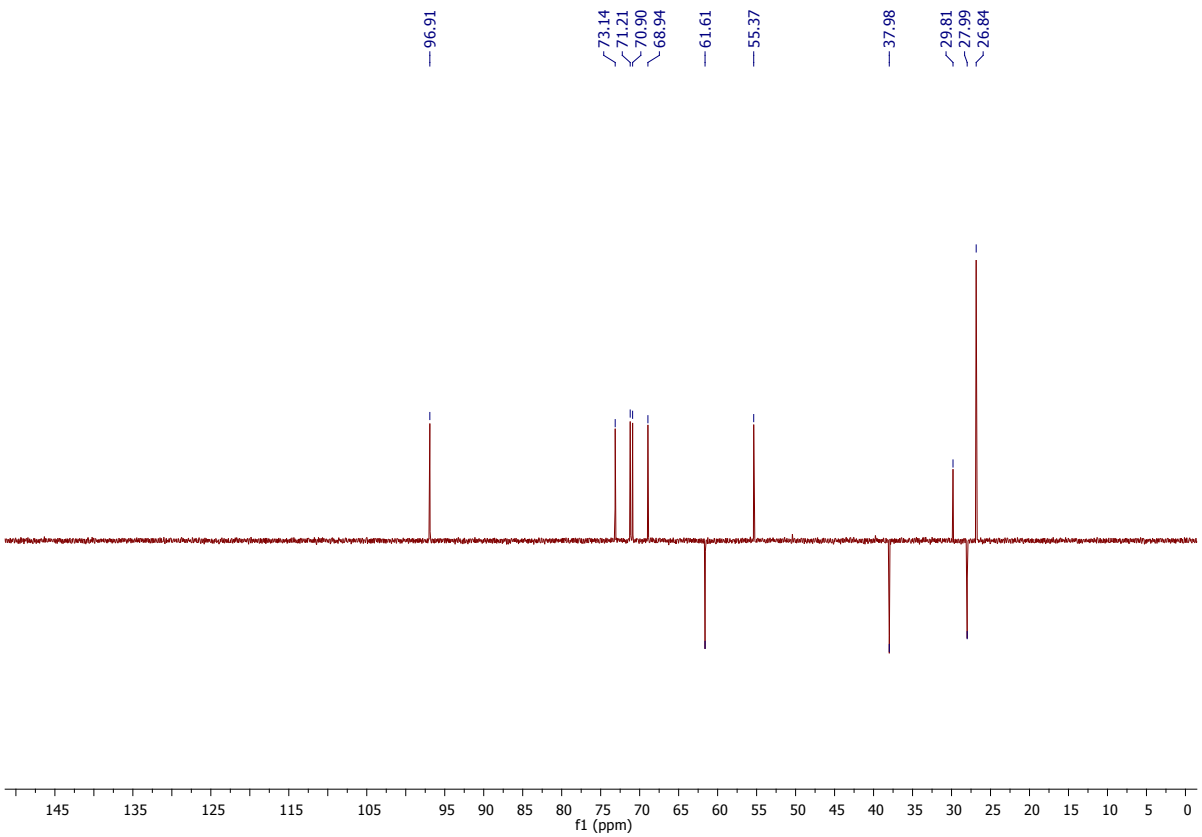




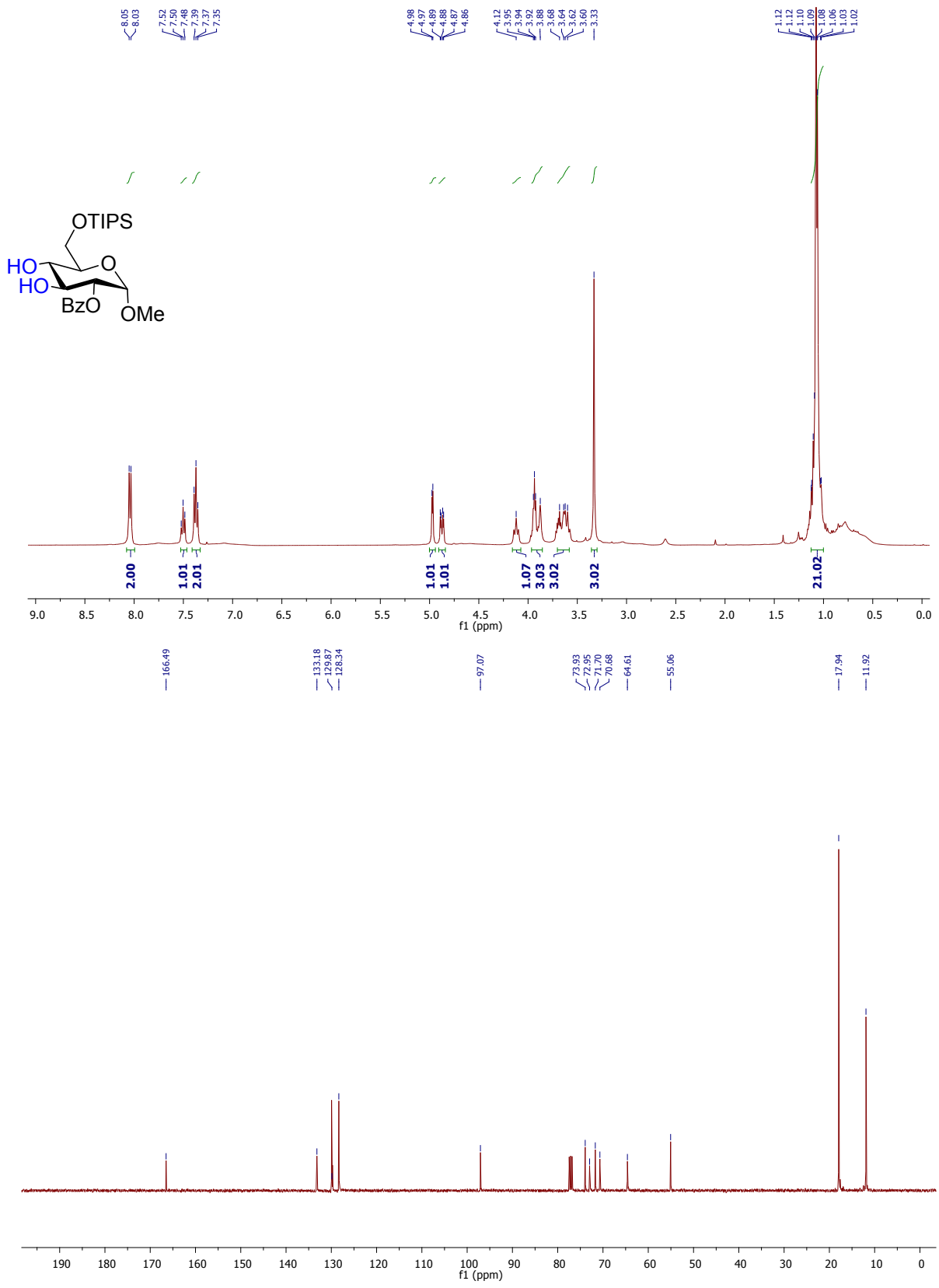
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2g ($CDCl_3$)

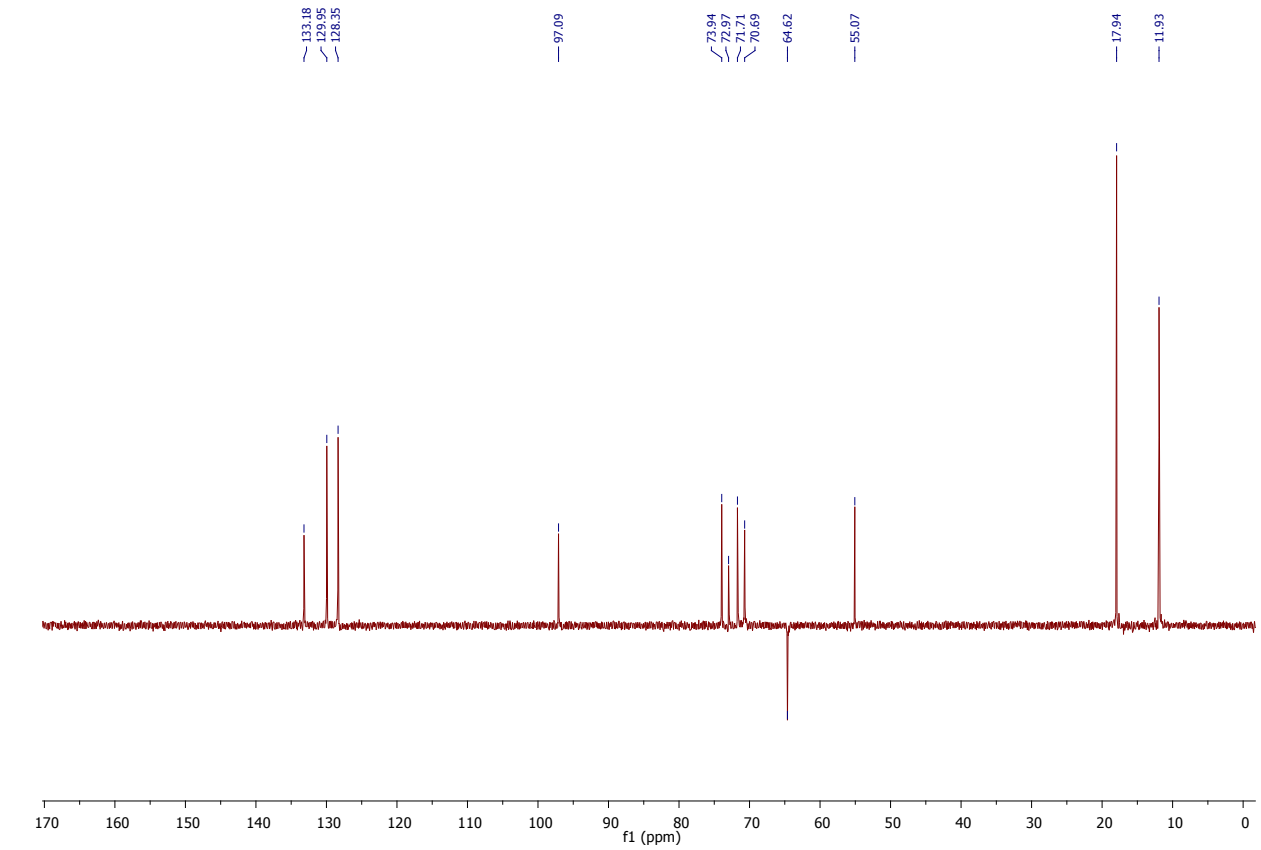



207.90
177.95
172.54
96.88
73.11
71.19
70.88
68.90
61.58
55.35
38.68
37.96
29.80
27.97
26.82
f1 (ppm)

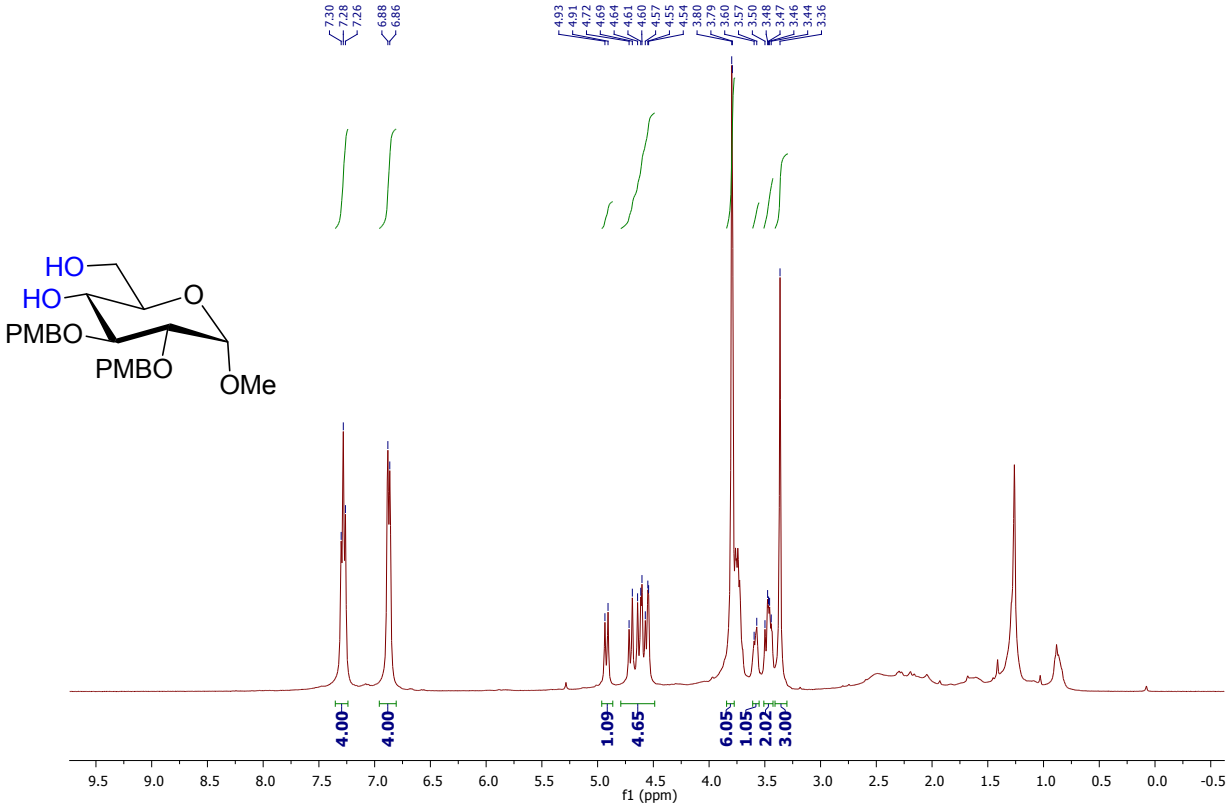

96.91
73.14
71.21
70.90
68.94
61.61
55.37
37.98
29.81
27.99
26.84
f1 (ppm)

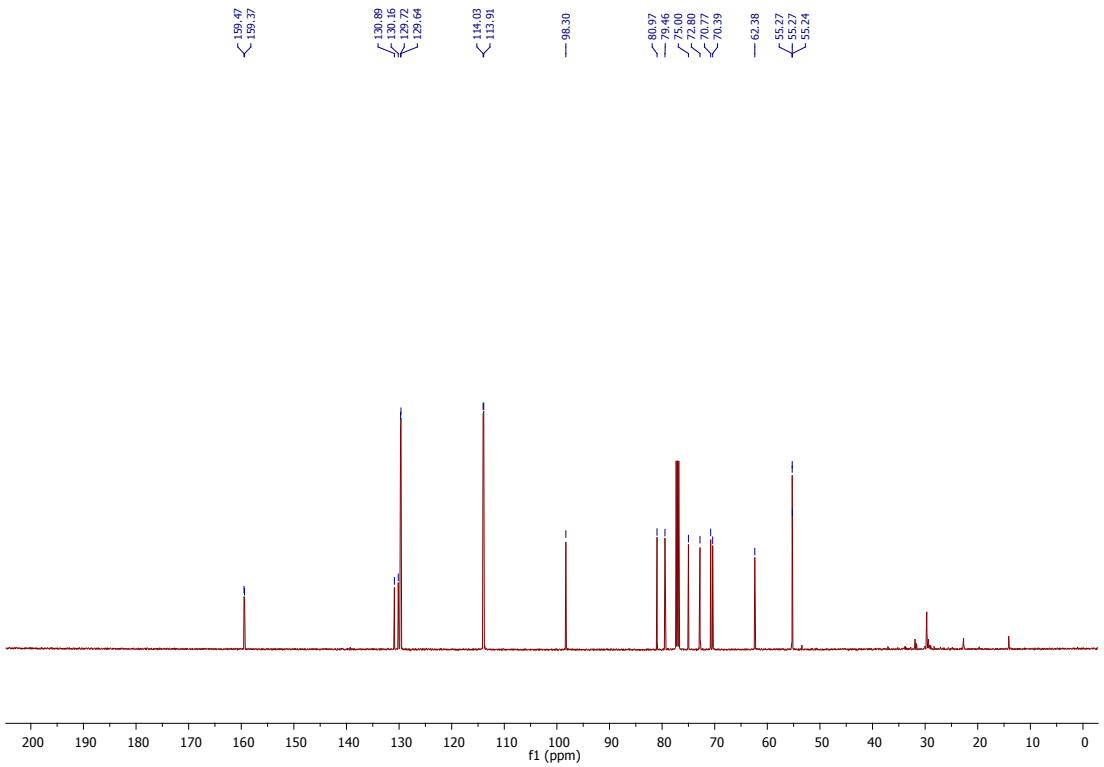
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2h ($CDCl_3$)



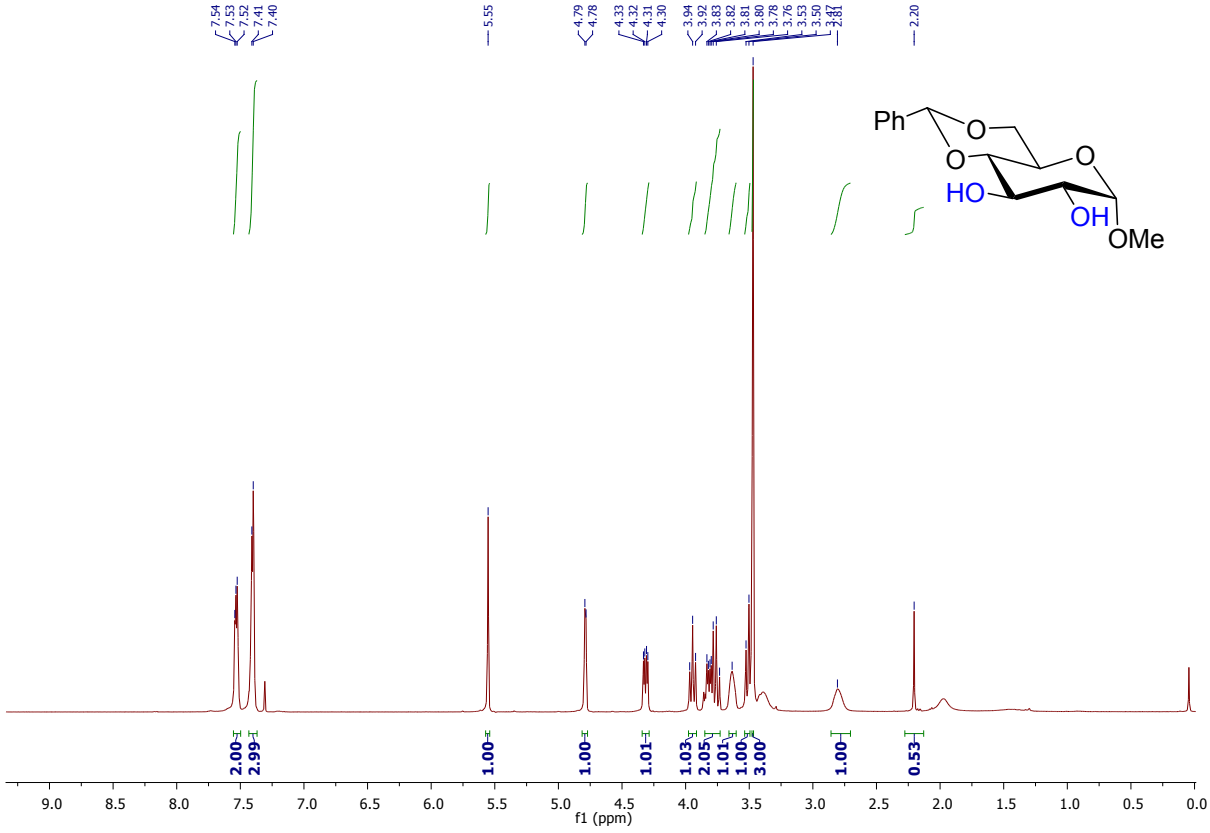


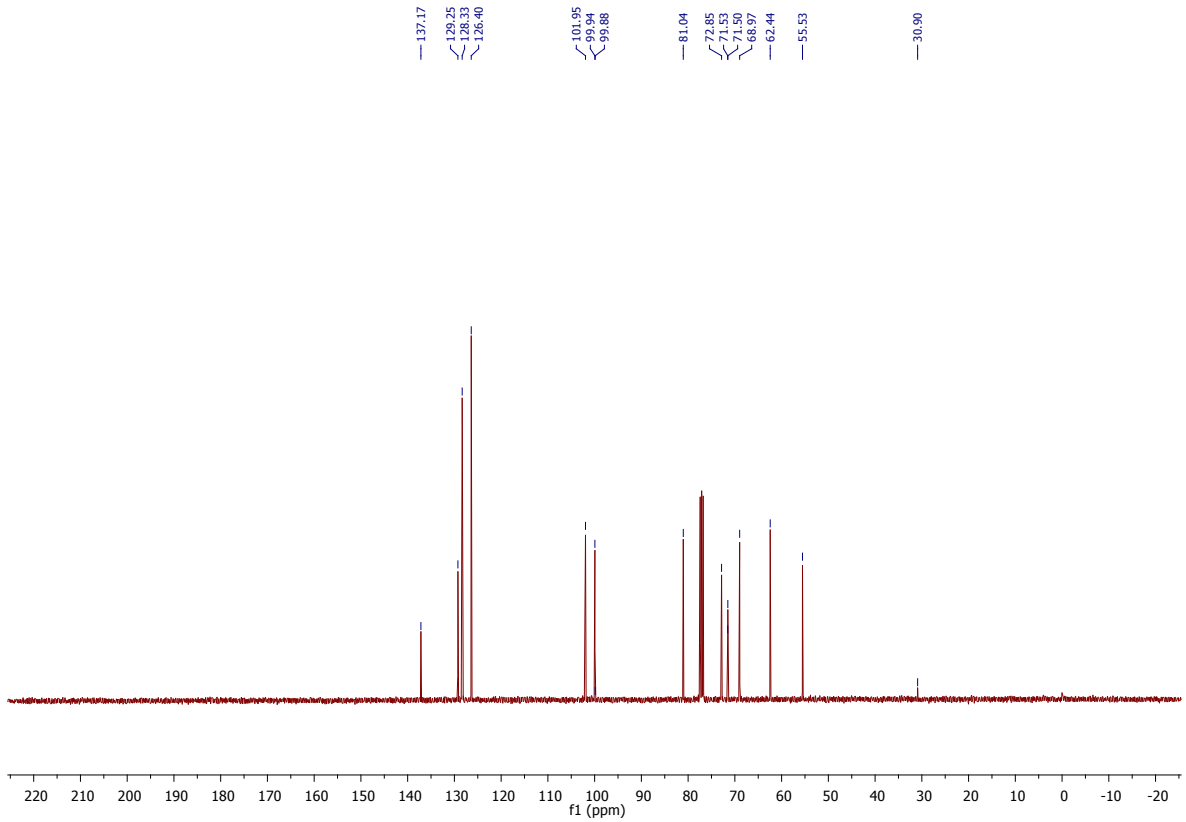
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2i ($CDCl_3$)

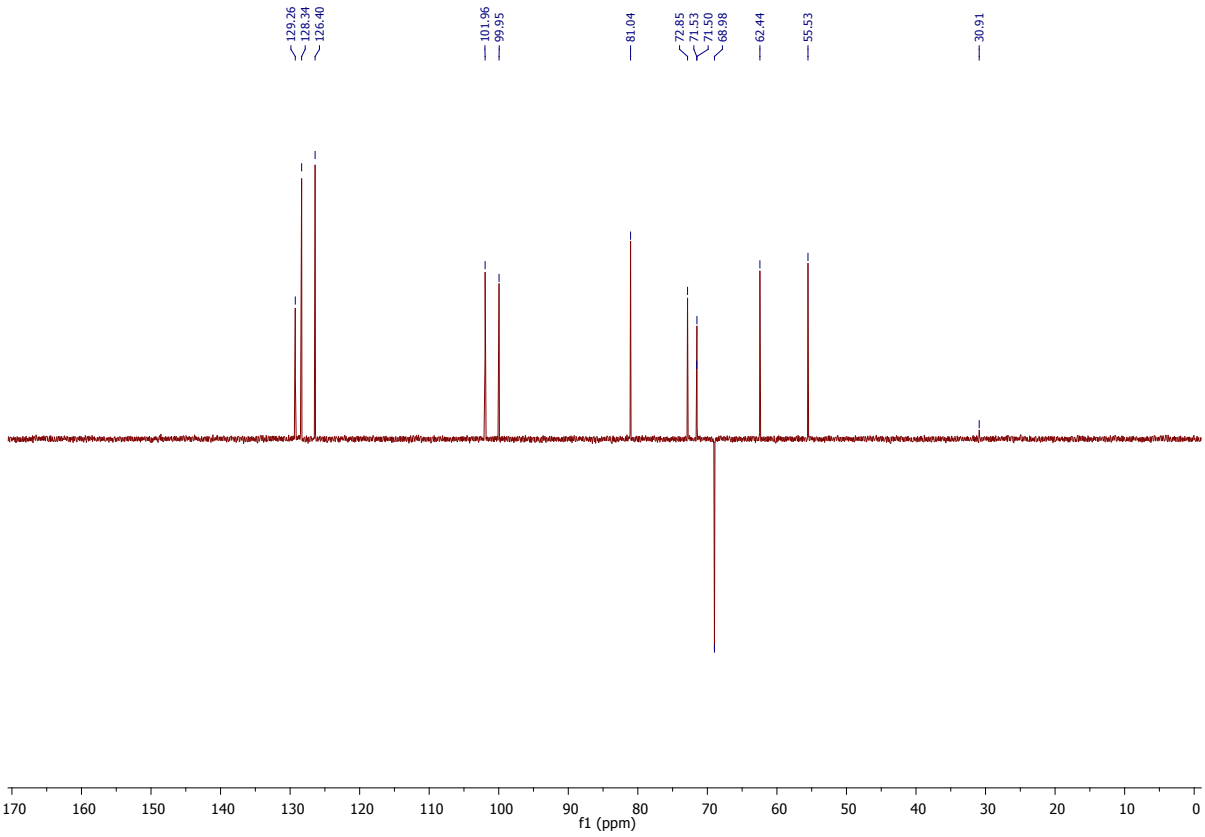




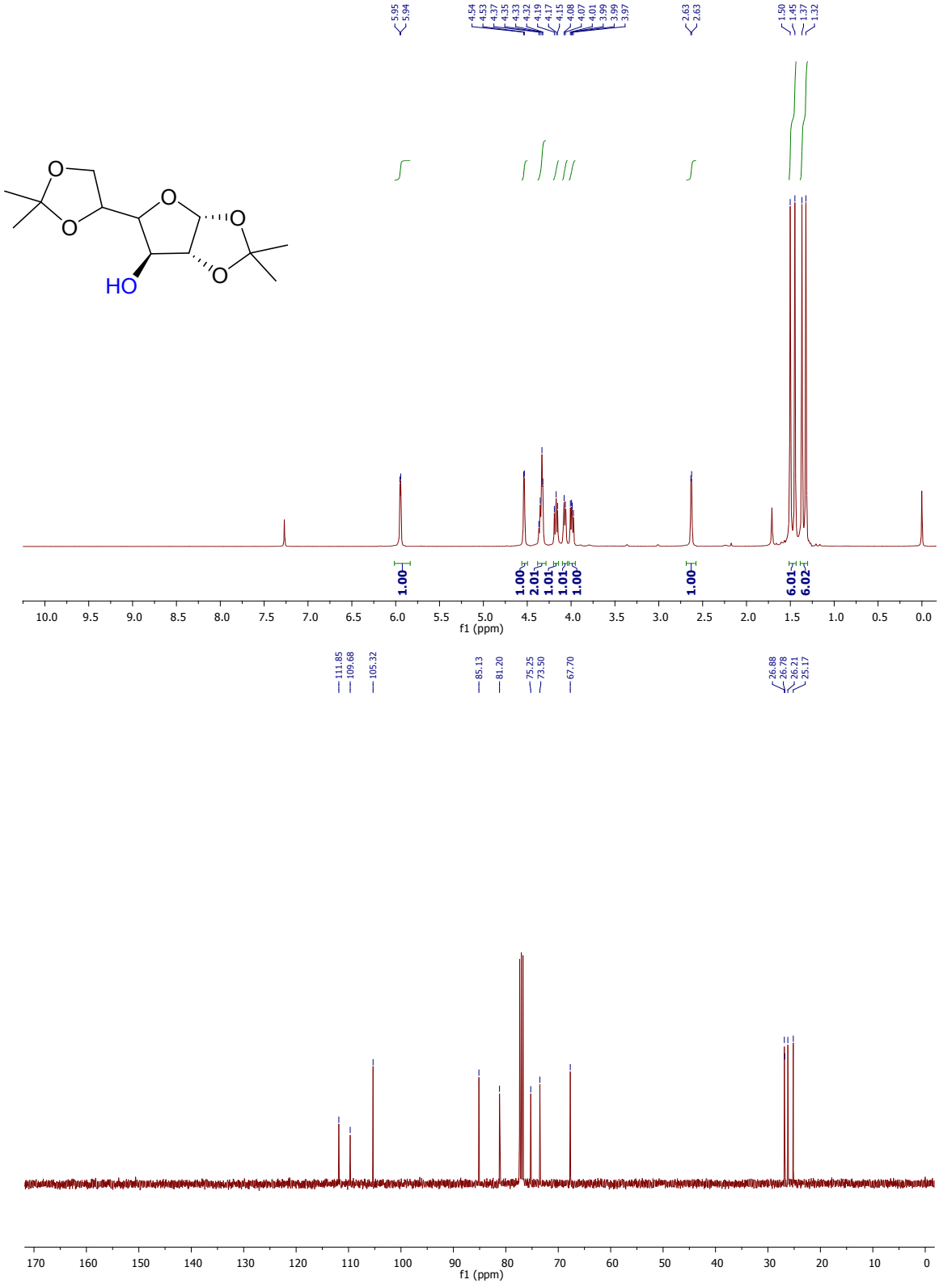
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2j ($CDCl_3$)

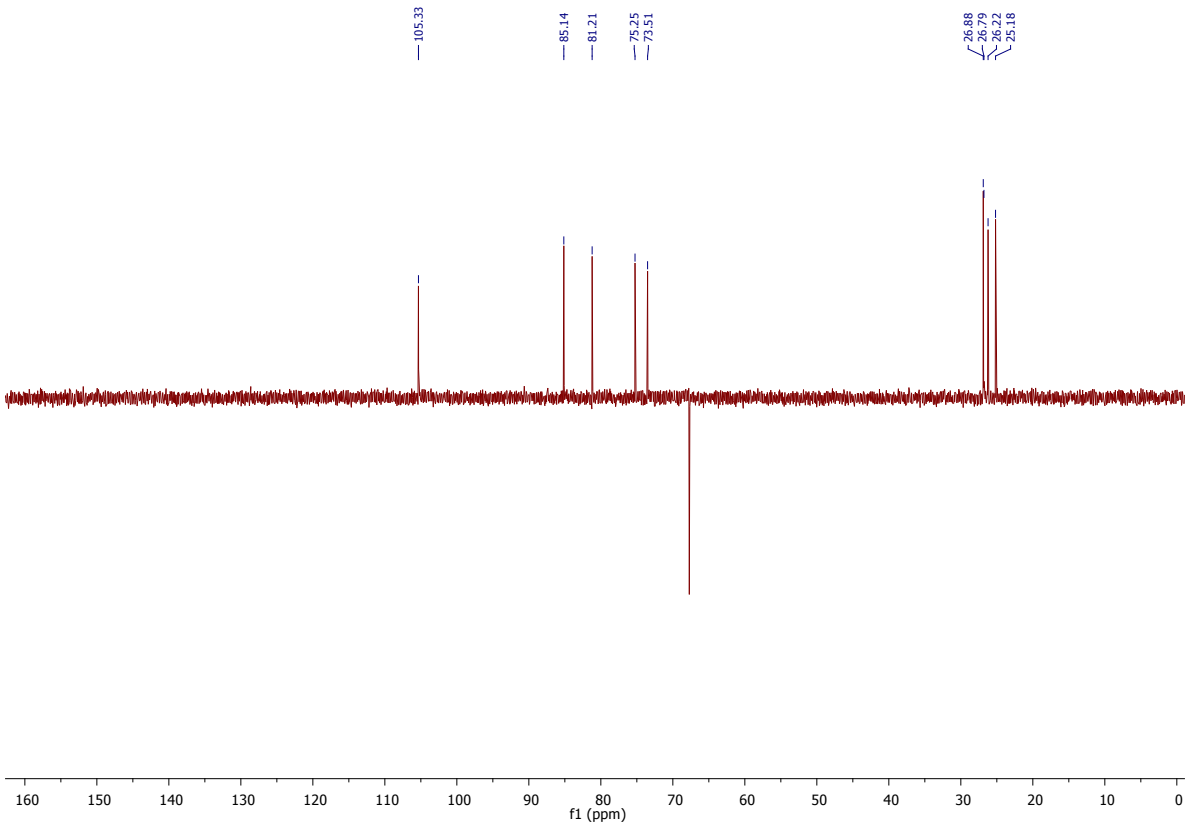



137.17
129.25
128.33
126.40
101.95
99.94
99.88
81.04
72.85
71.53
71.50
68.97
62.44
55.53
30.90
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

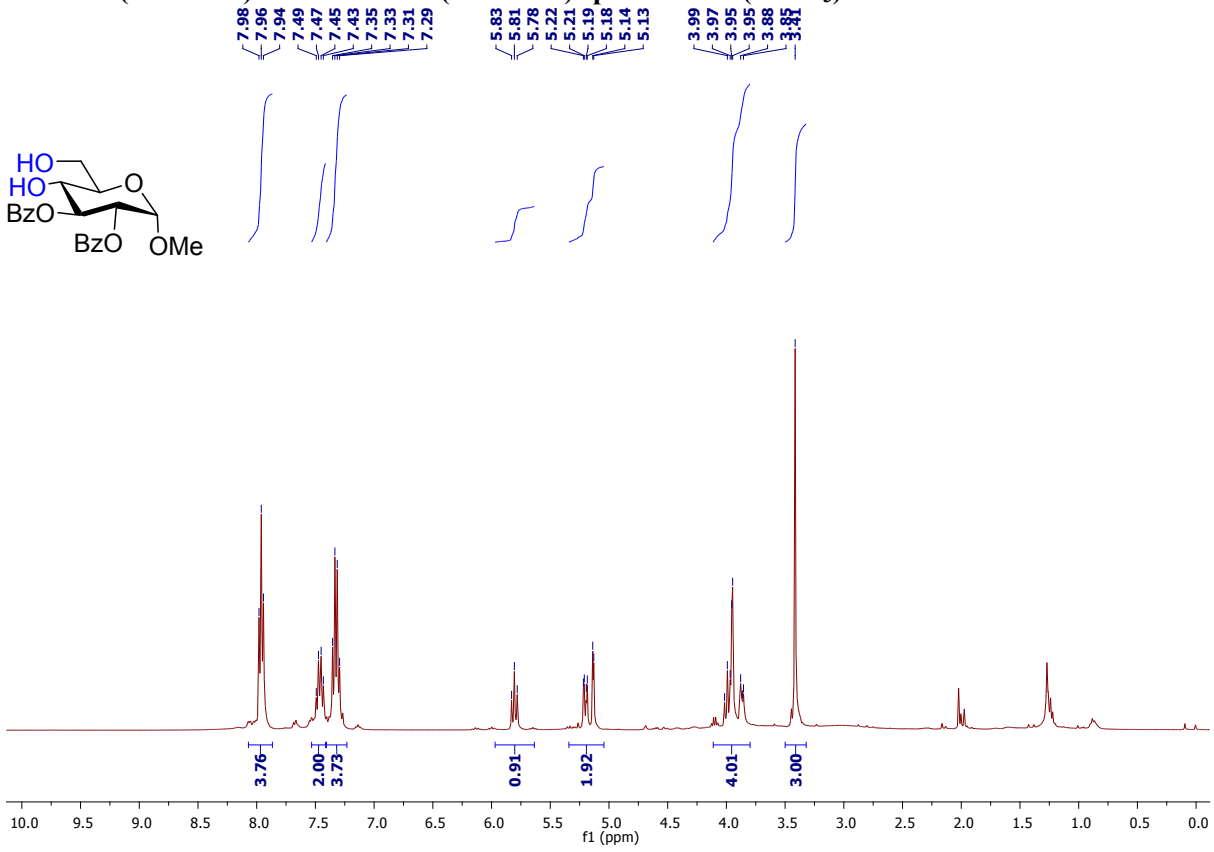

129.26
128.34
126.40
101.96
99.95
81.04
72.85
71.53
71.50
68.98
62.44
55.53
30.91
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

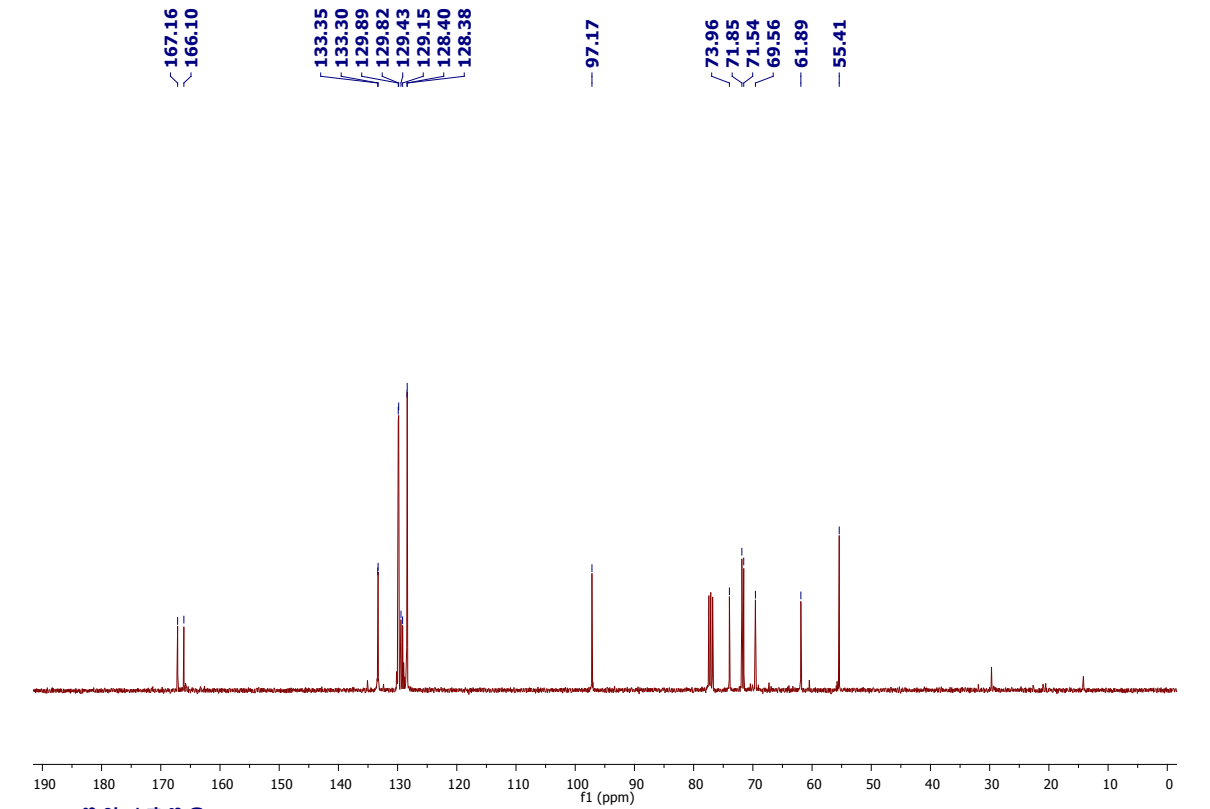
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2k ($CDCl_3$)

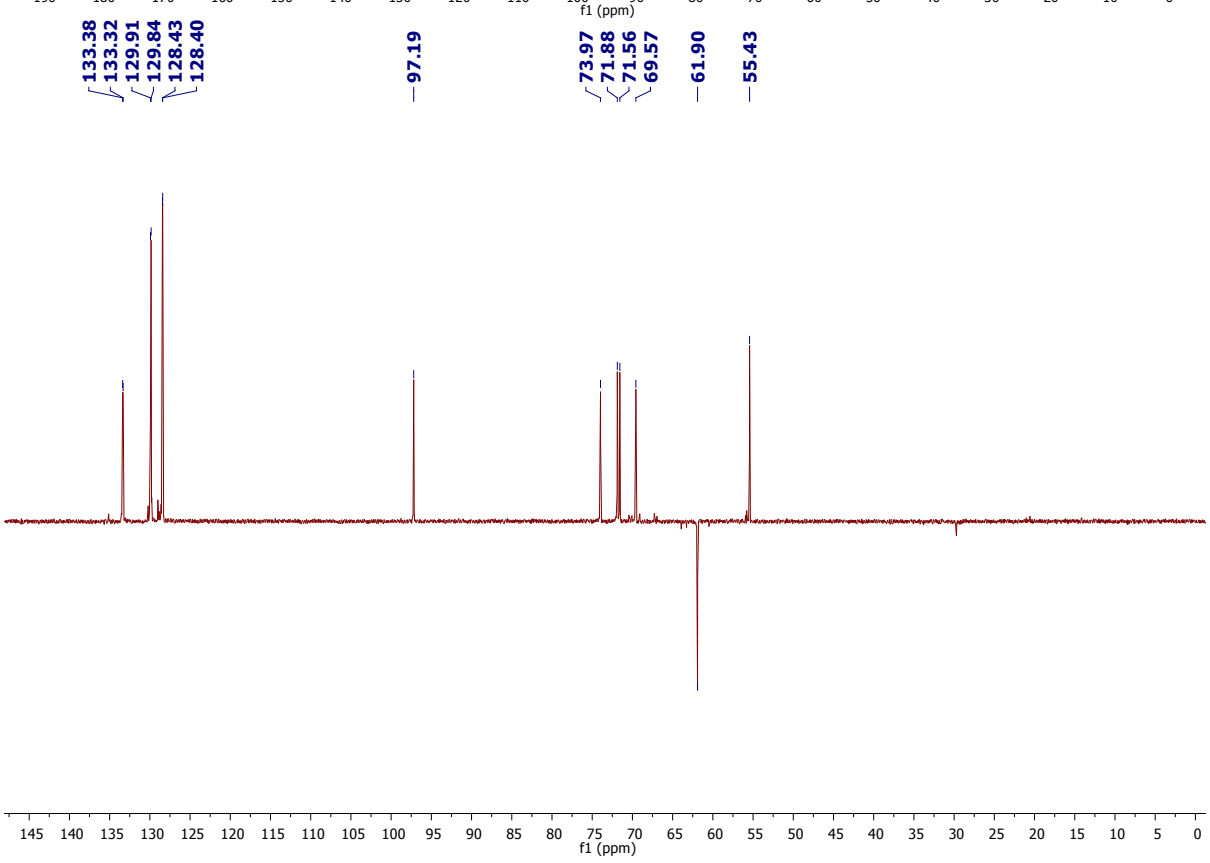




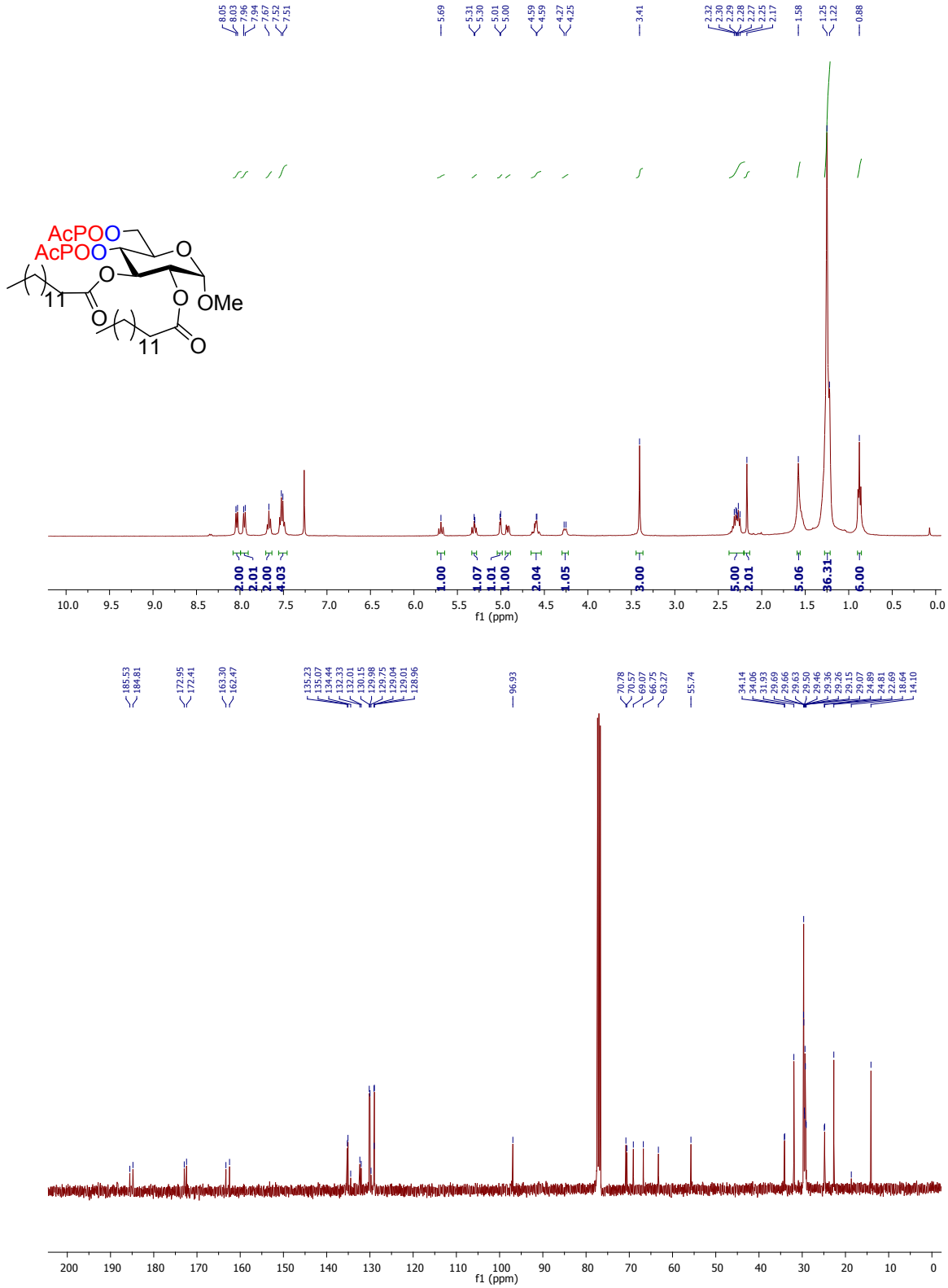
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 2l ($CDCl_3$)



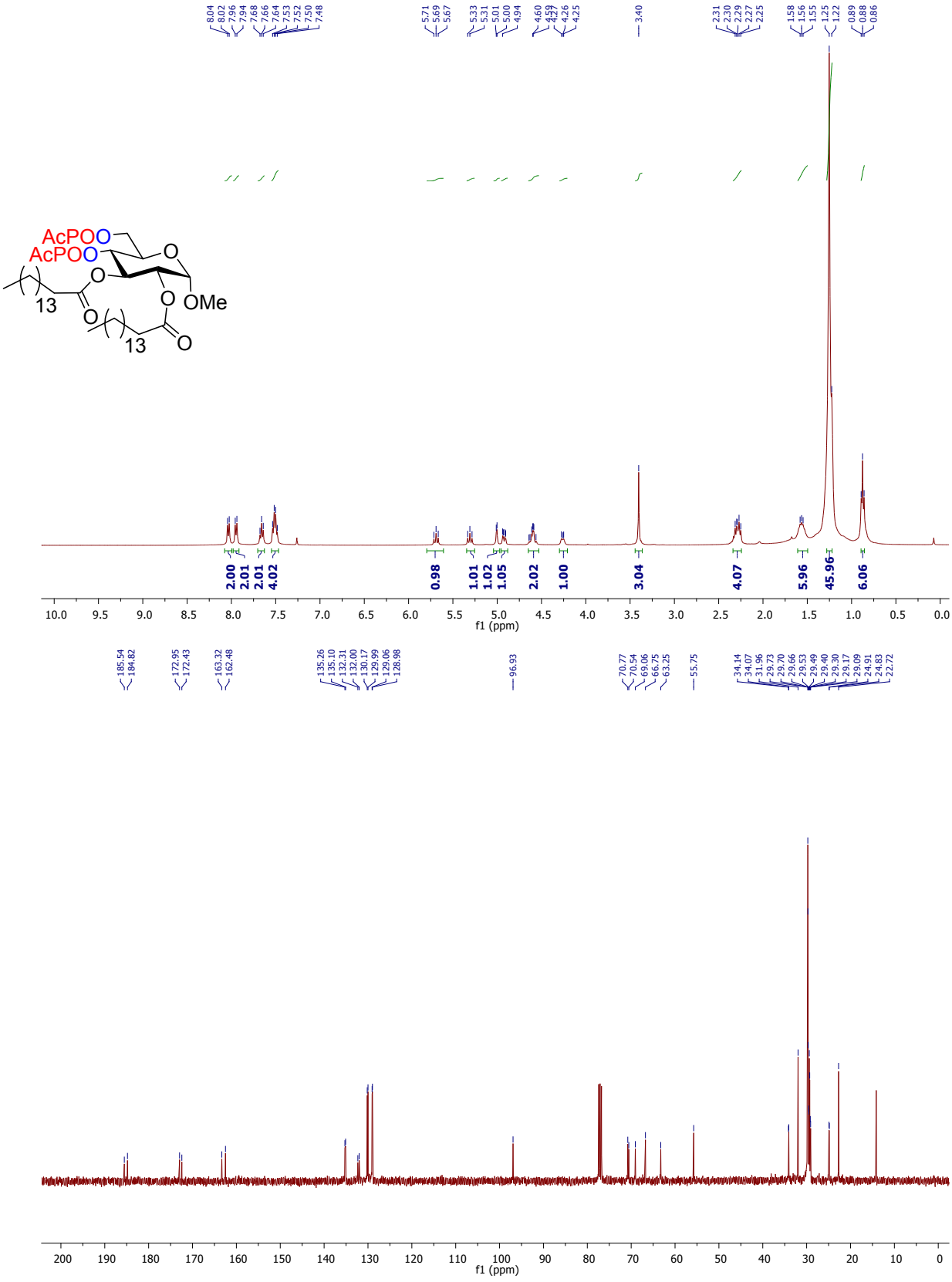

167.16
166.10
133.35
133.30
129.89
129.82
129.43
129.15
128.40
128.38
97.17
73.96
71.85
71.54
69.56
61.89
55.41
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

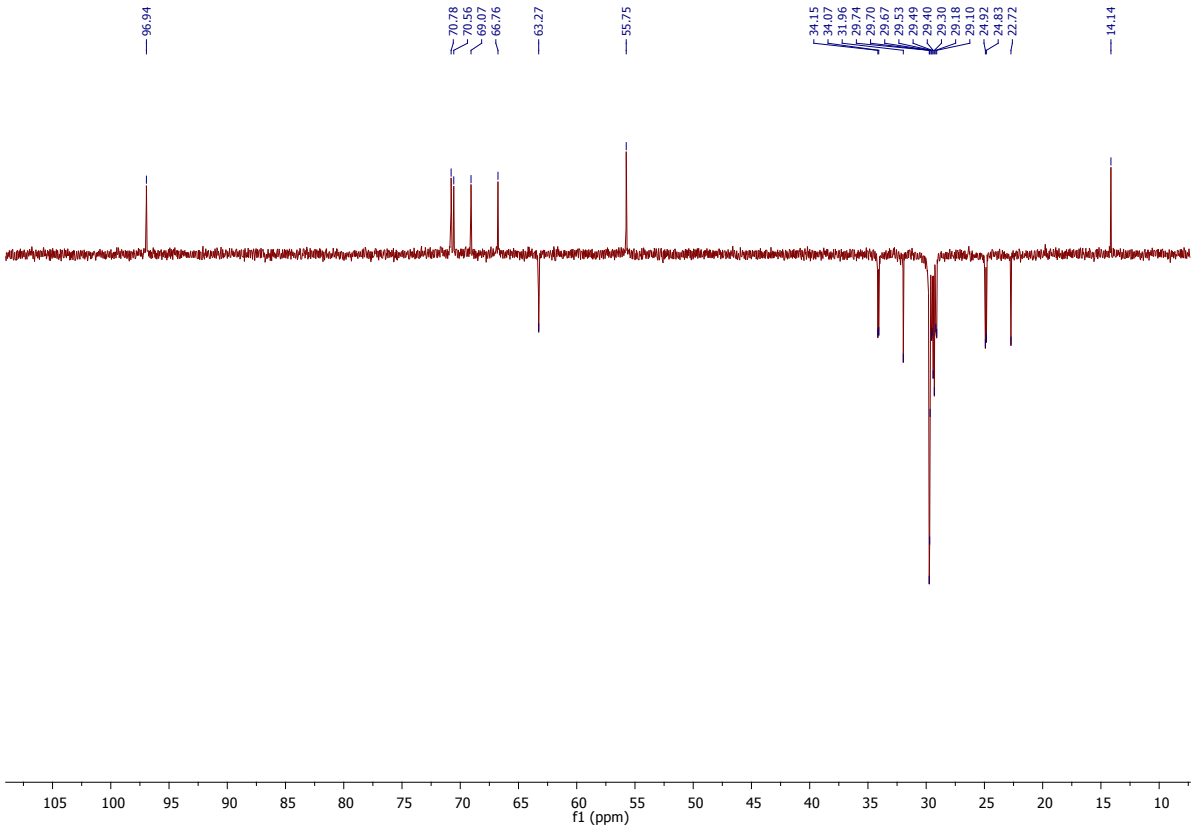

133.38
133.32
129.91
129.84
128.43
128.40
97.19
73.97
71.88
71.56
69.57
61.90
55.43
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3a ($CDCl_3$)

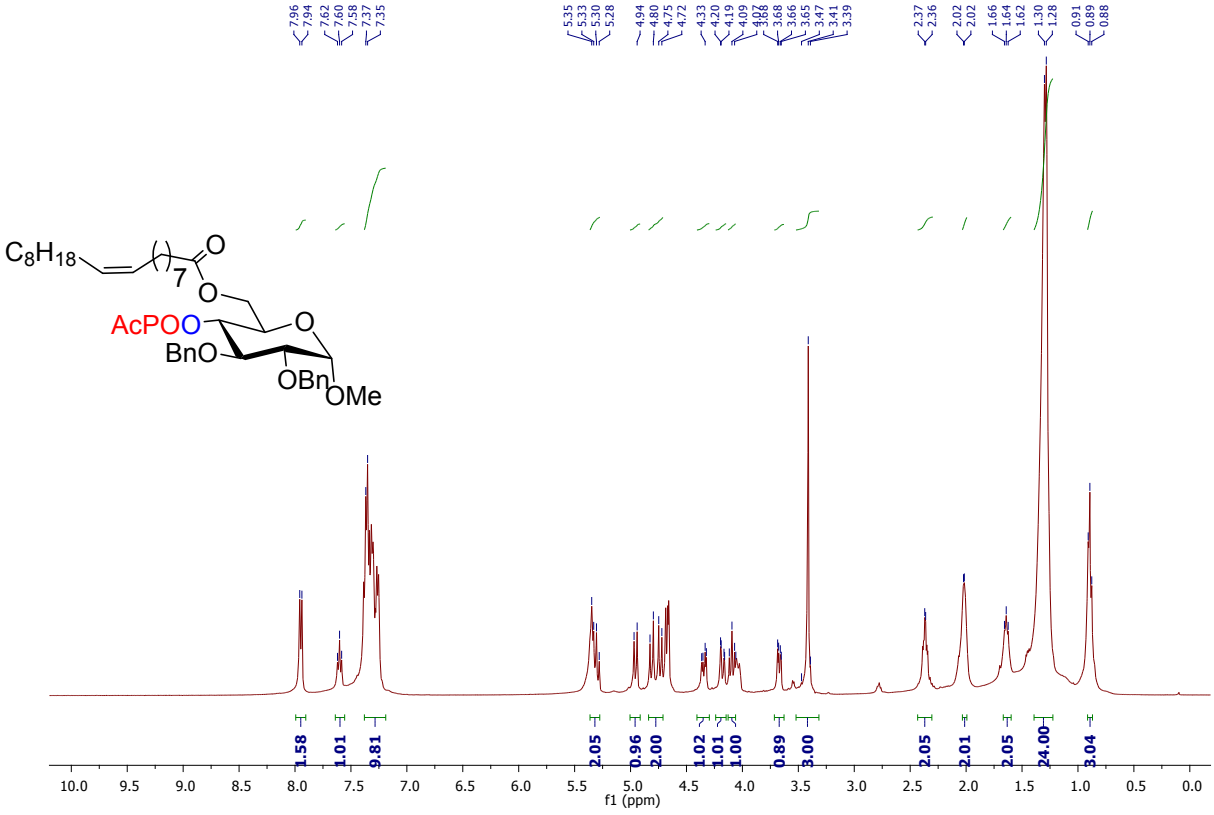


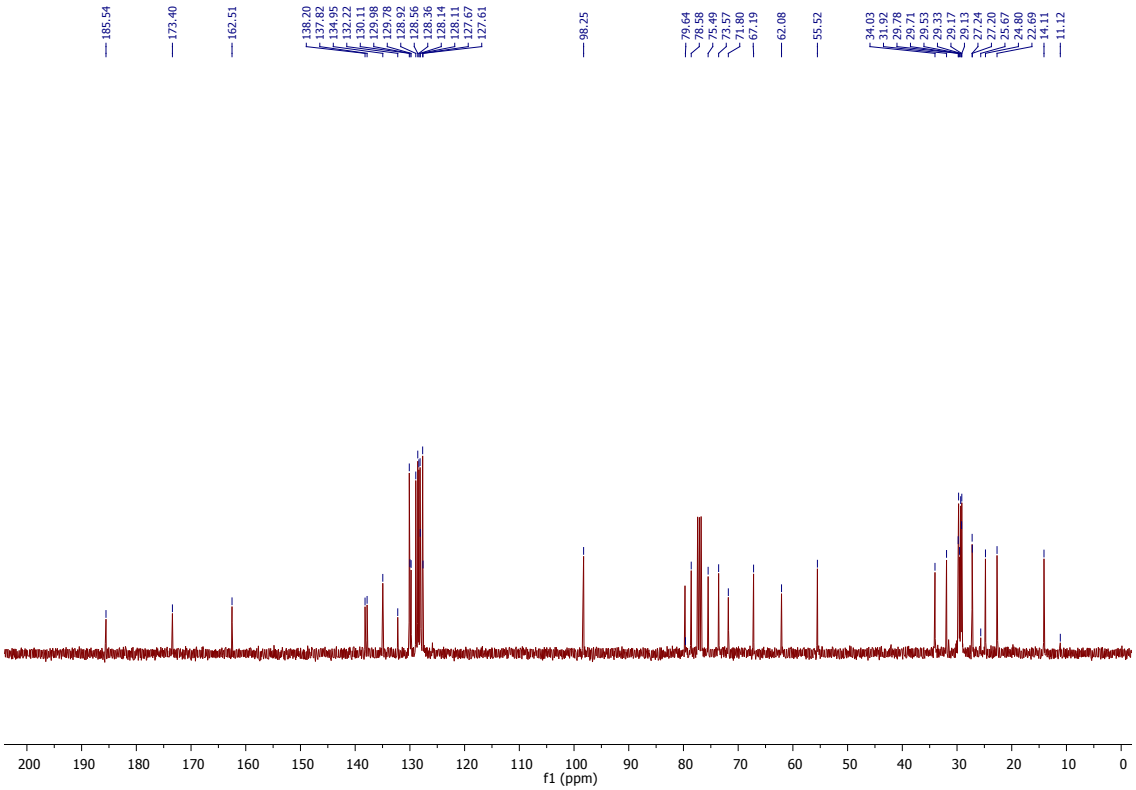
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3b ($CDCl_3$)



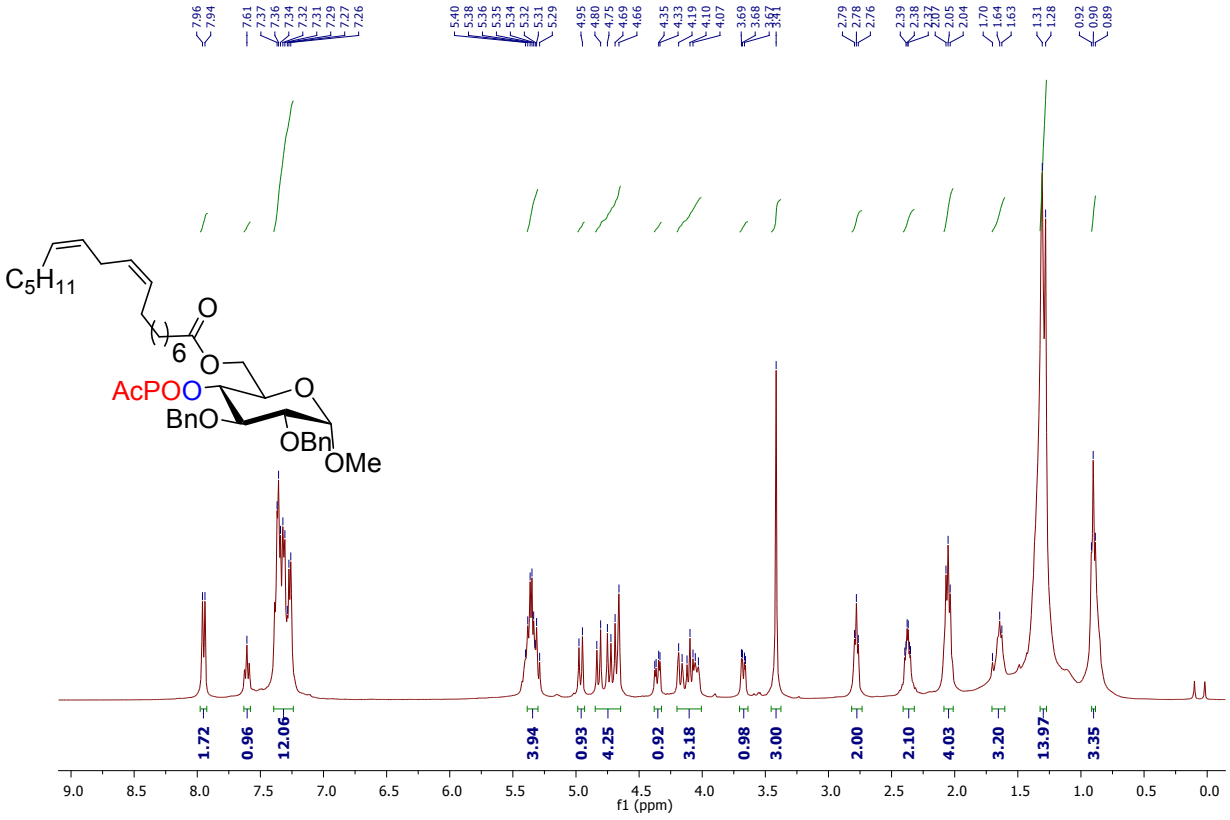


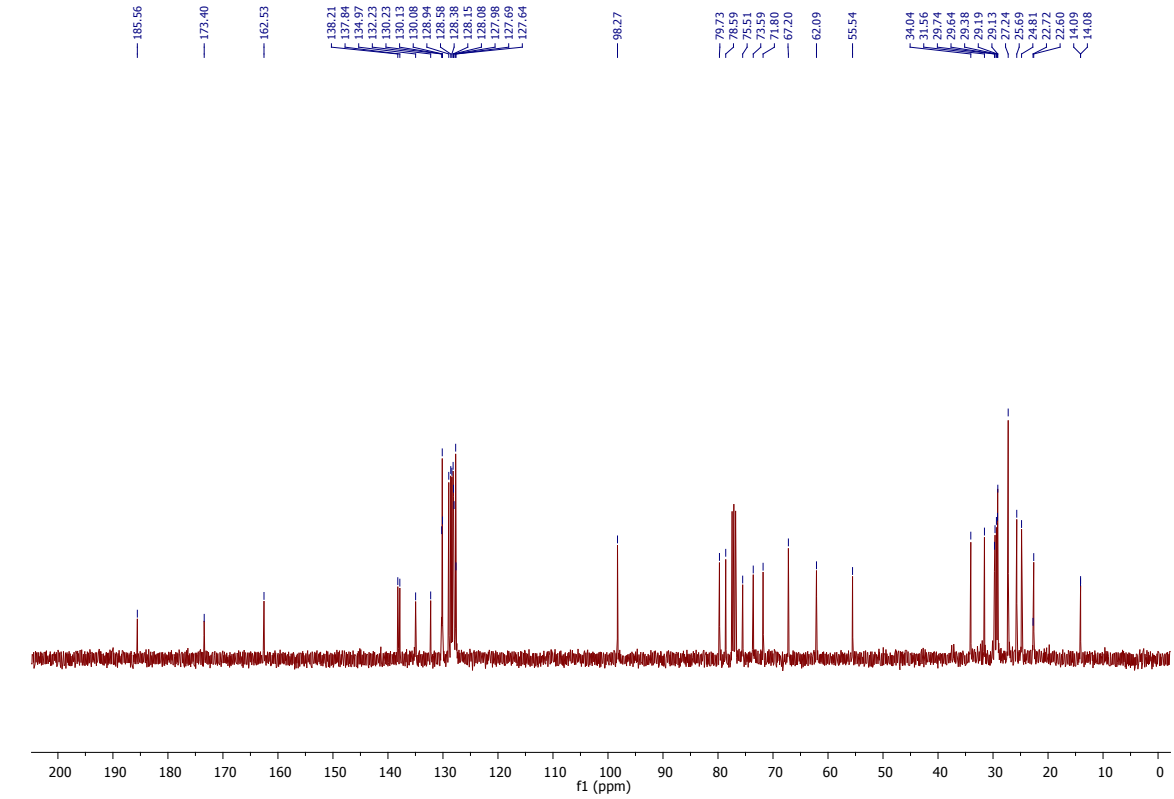
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3c ($CDCl_3$)



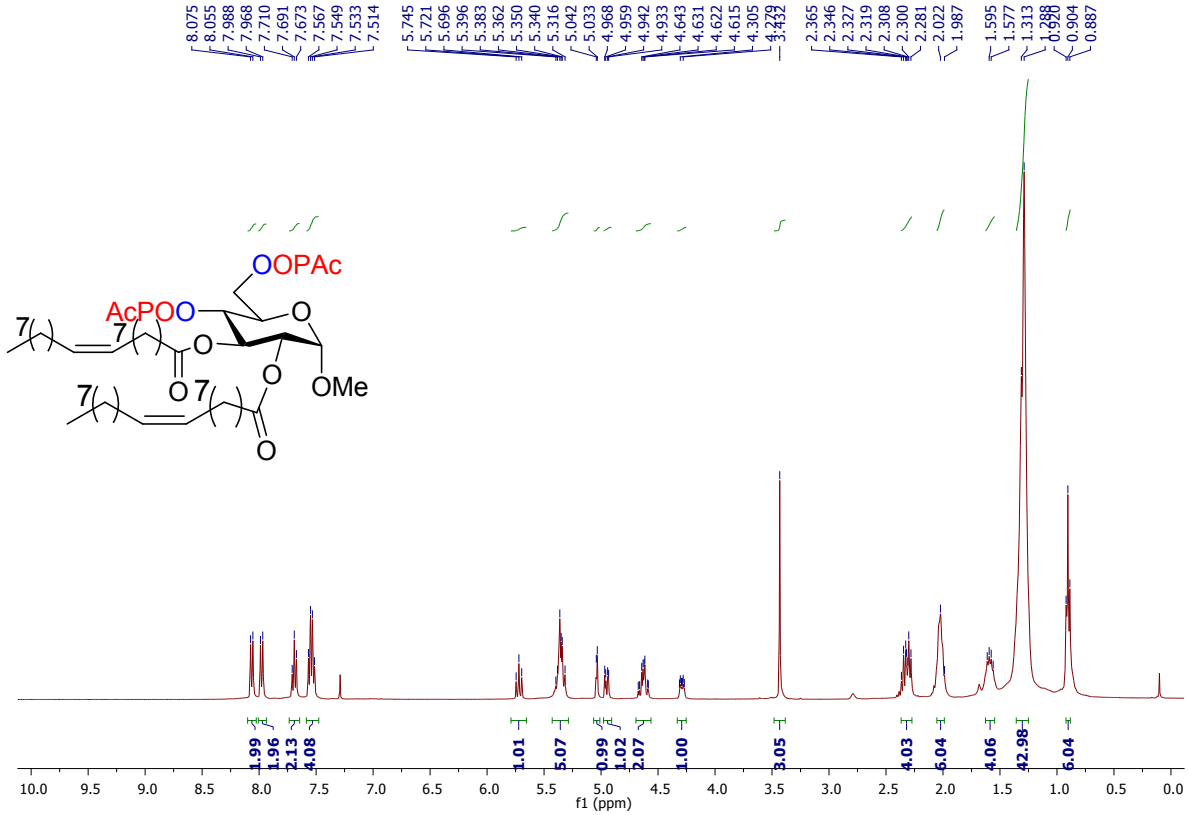


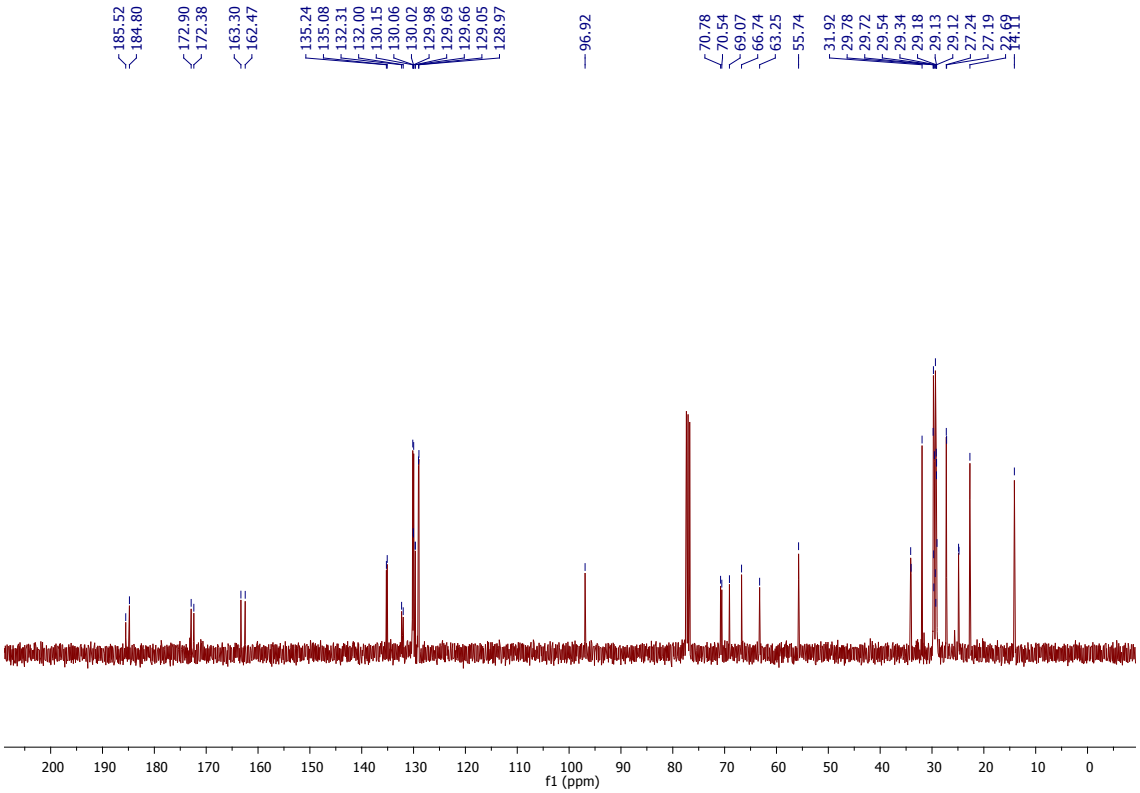
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3d ($CDCl_3$)



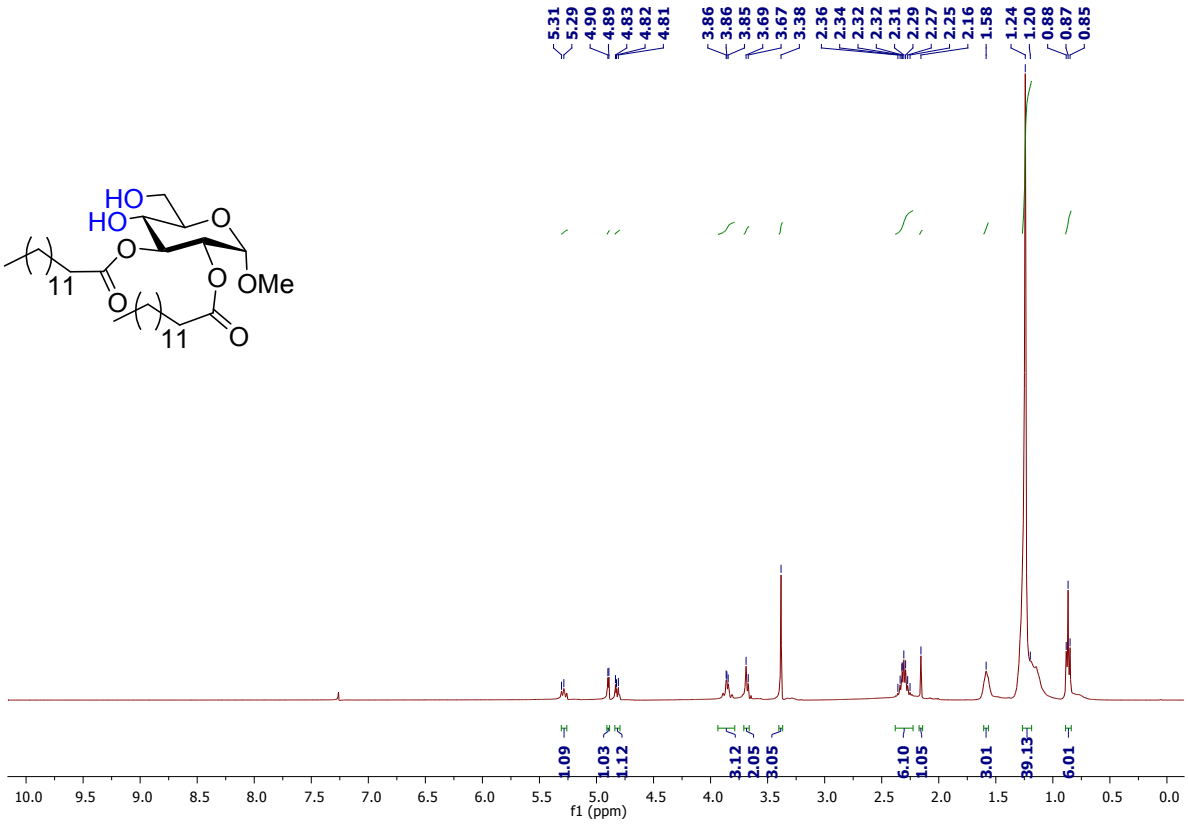


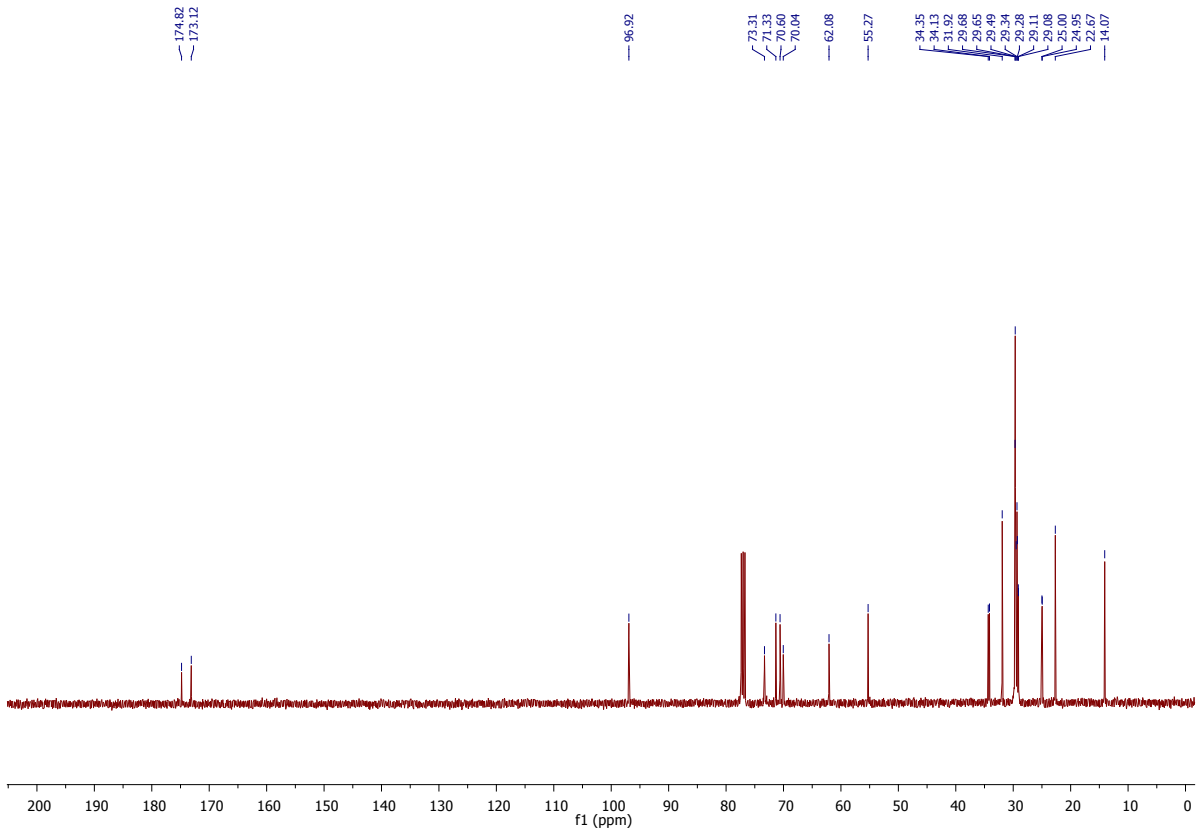
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 3e ($CDCl_3$)

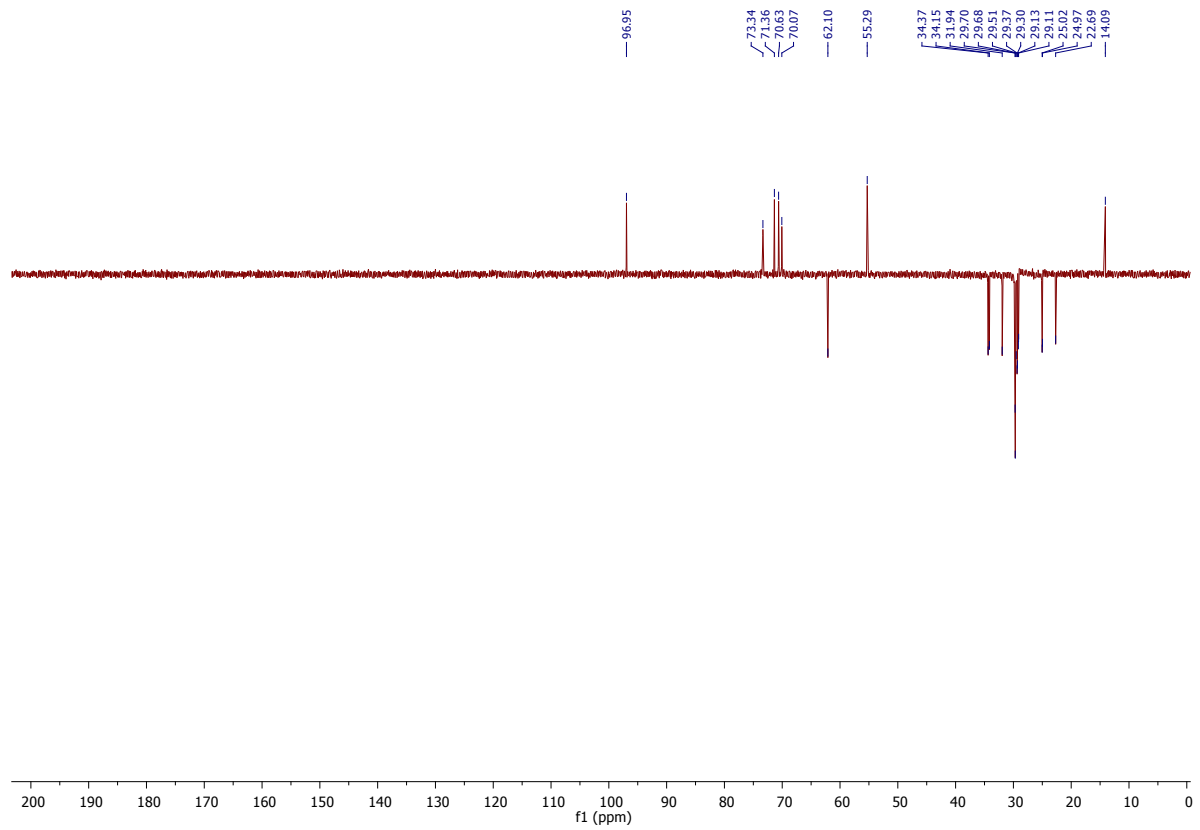




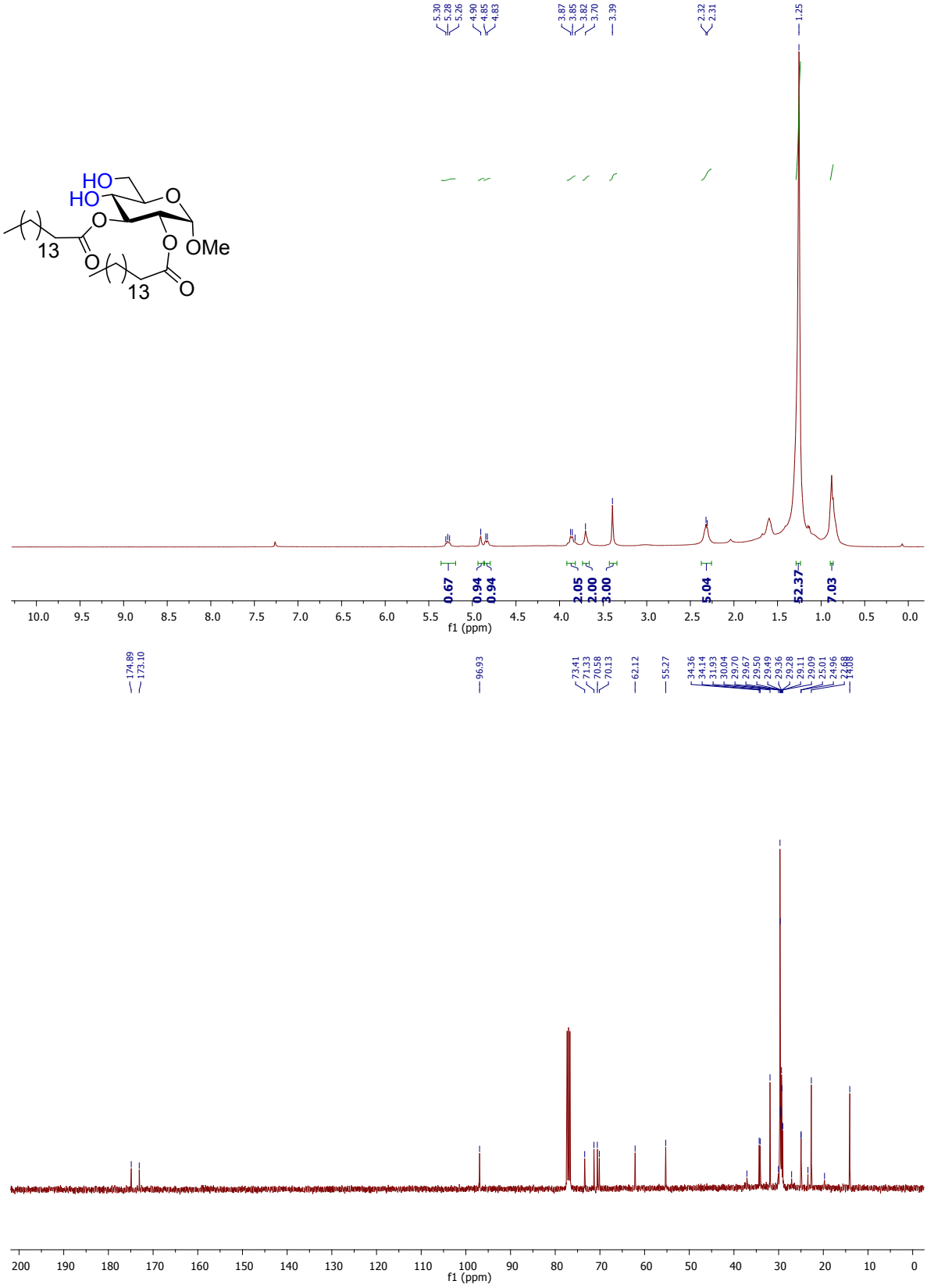
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4a ($CDCl_3$)



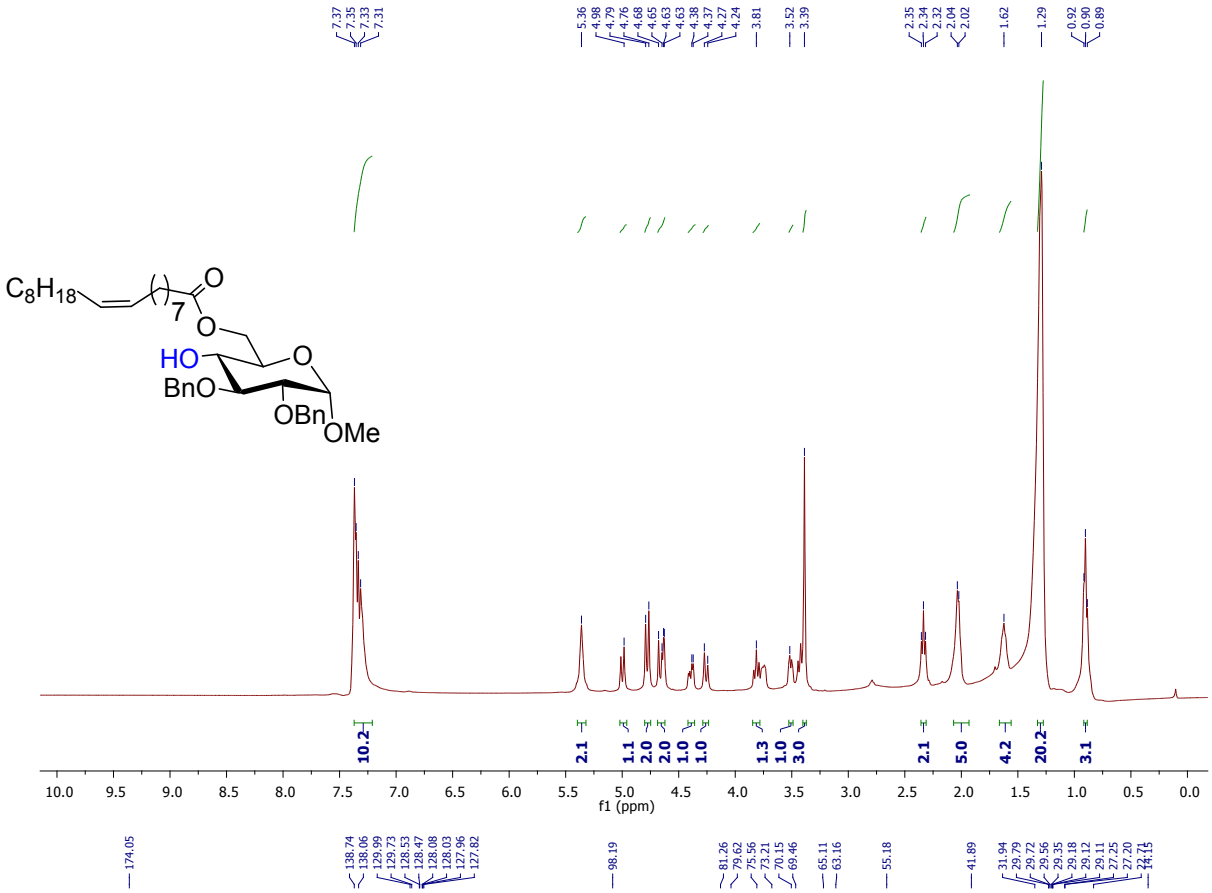

174.82
173.12
96.92
73.31
71.33
70.60
70.04
62.08
55.27
34.35
34.13
31.92
29.68
29.65
29.49
29.34
29.28
29.11
29.08
25.00
24.95
22.67
14.07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

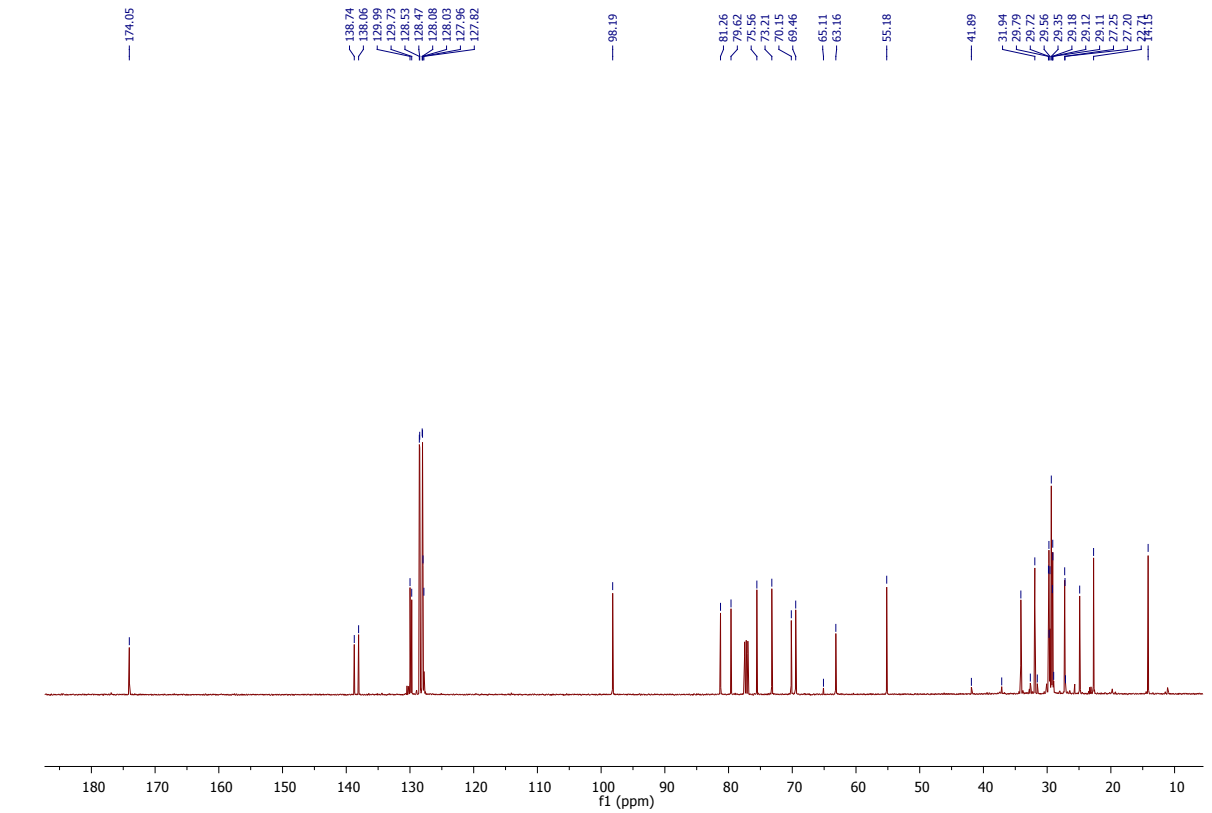

96.95
73.34
71.36
70.63
70.07
62.10
55.29
34.37
34.15
31.94
29.70
29.68
29.51
29.37
29.30
29.13
29.11
25.02
24.97
22.69
14.09
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4b ($CDCl_3$)

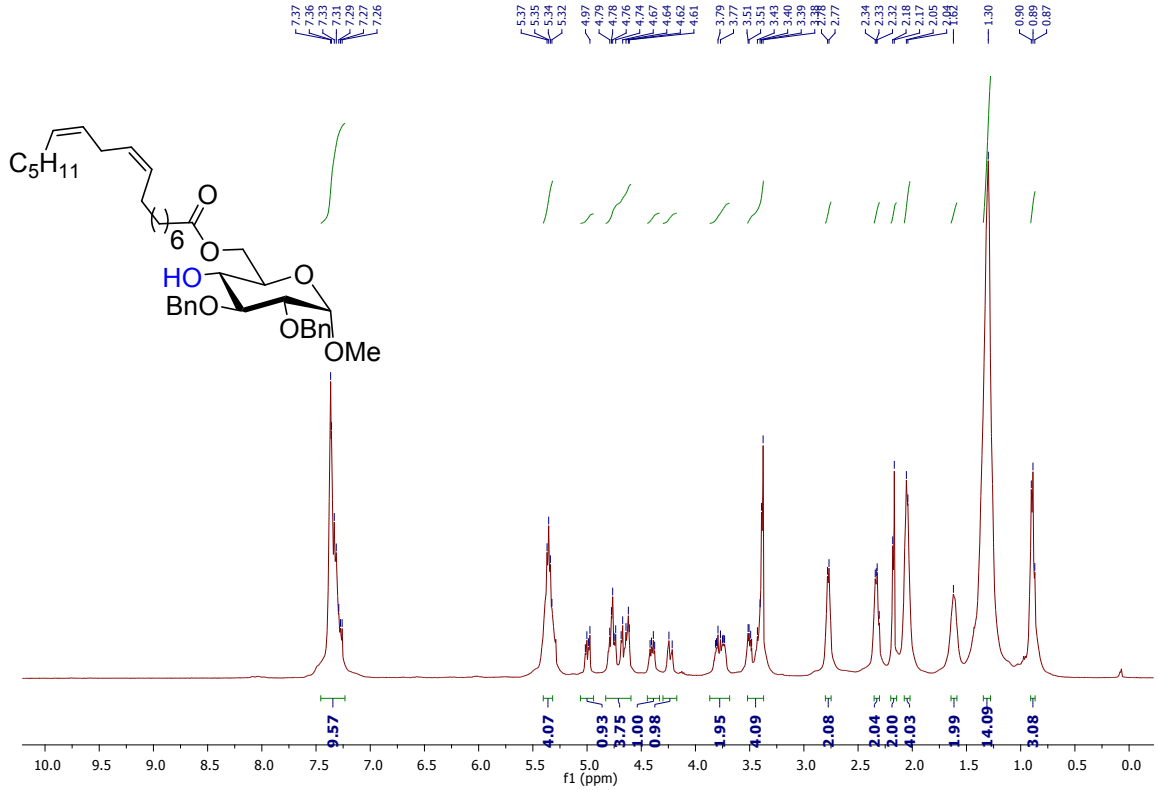


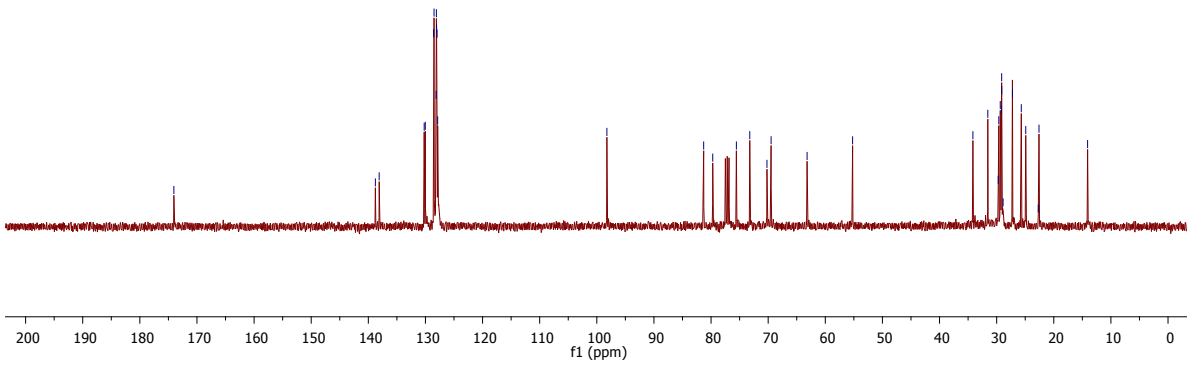
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4c ($CDCl_3$)

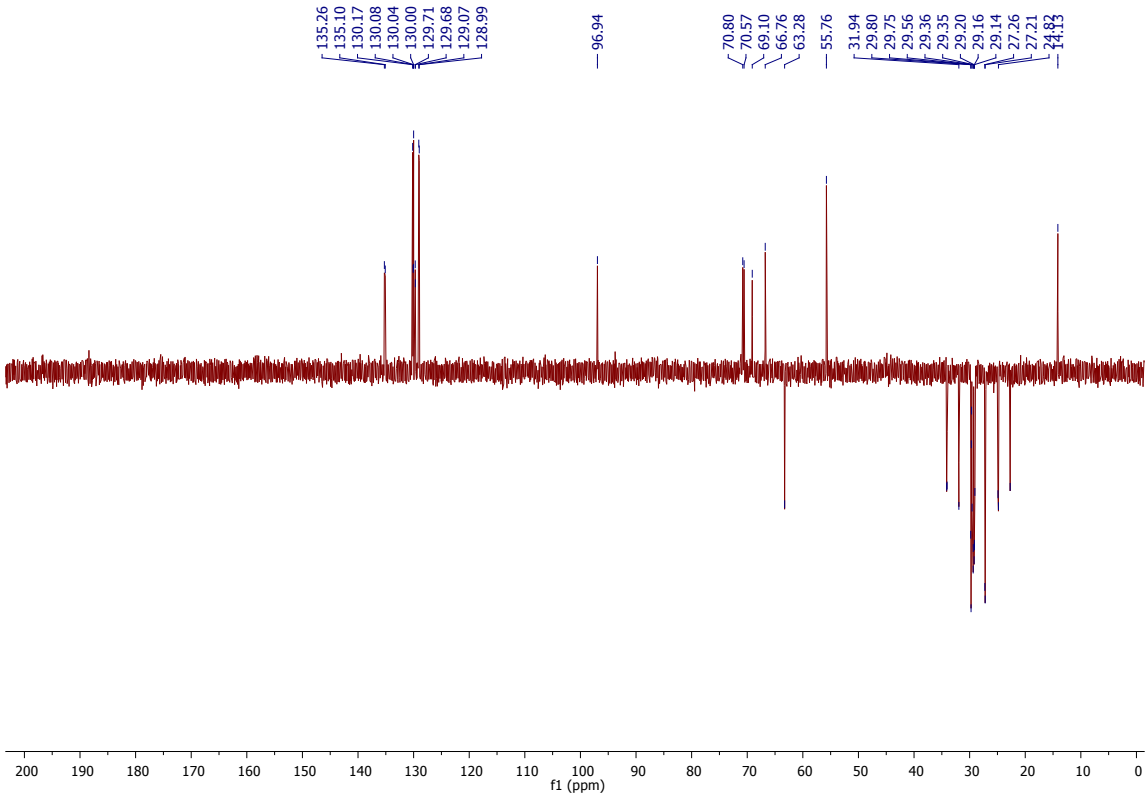




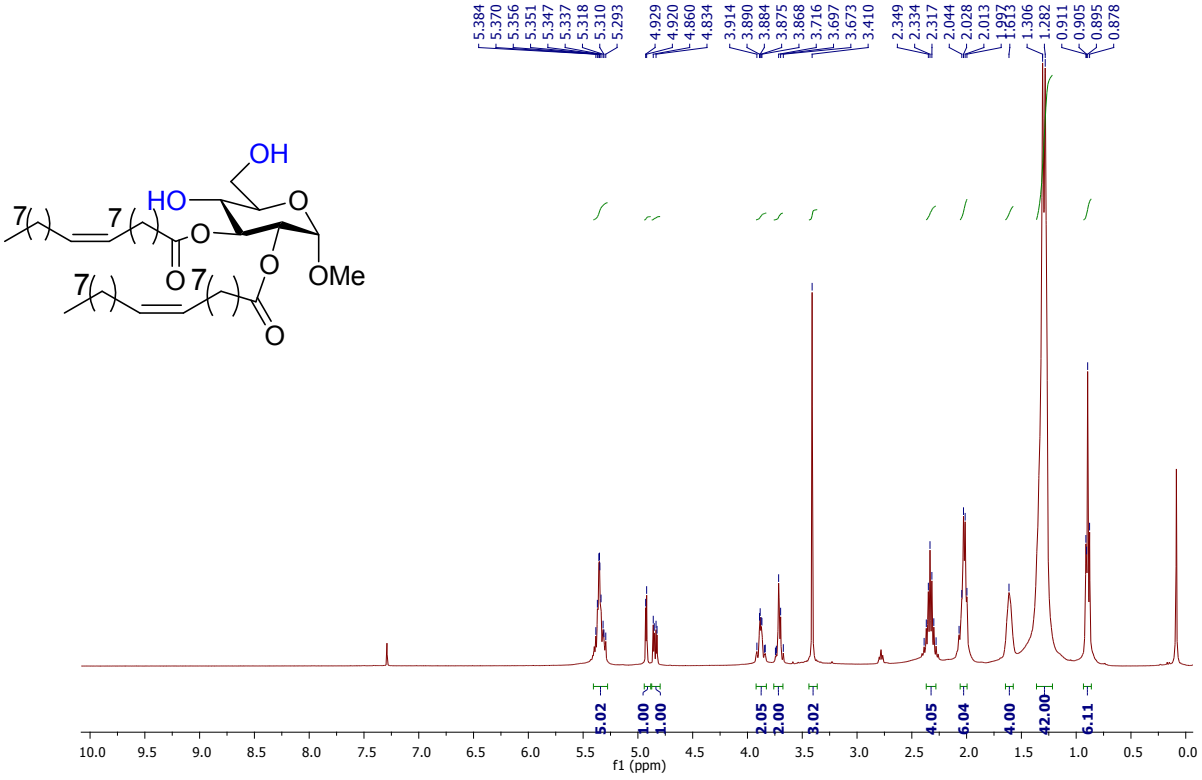
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4d ($CDCl_3$)

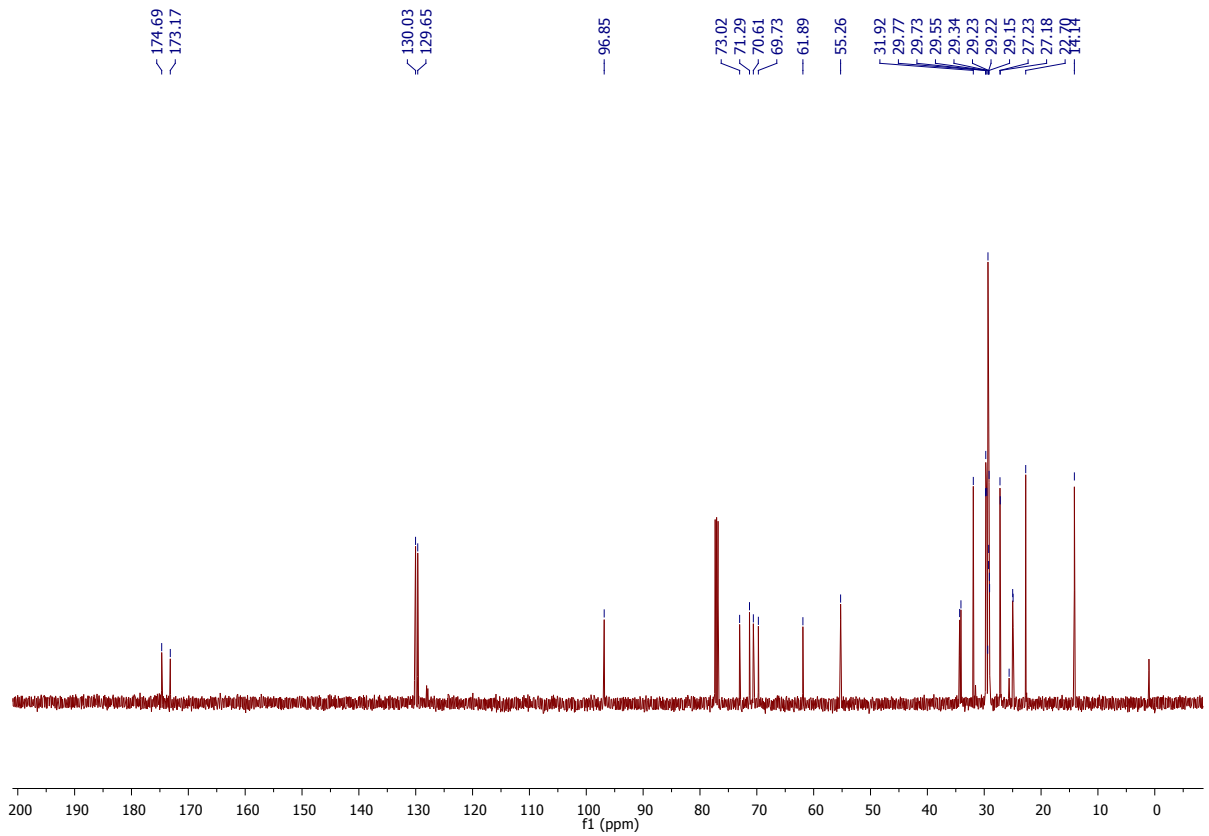




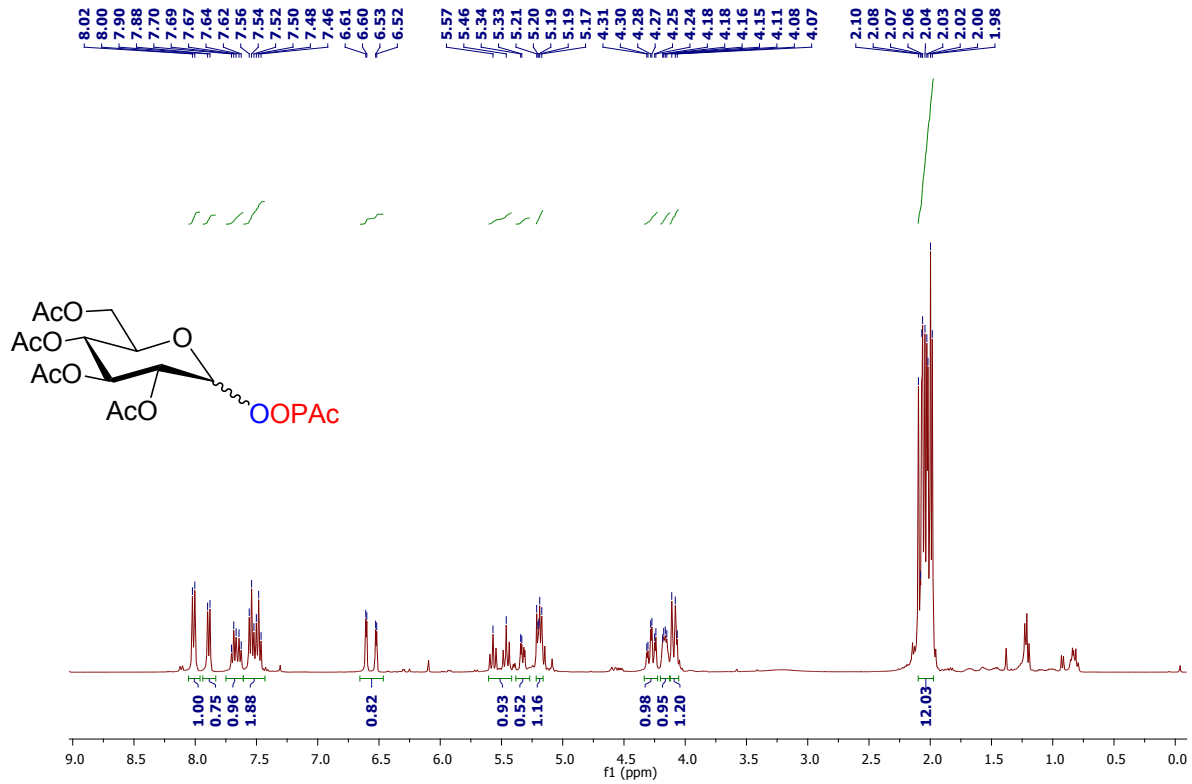


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 4e ($CDCl_3$)

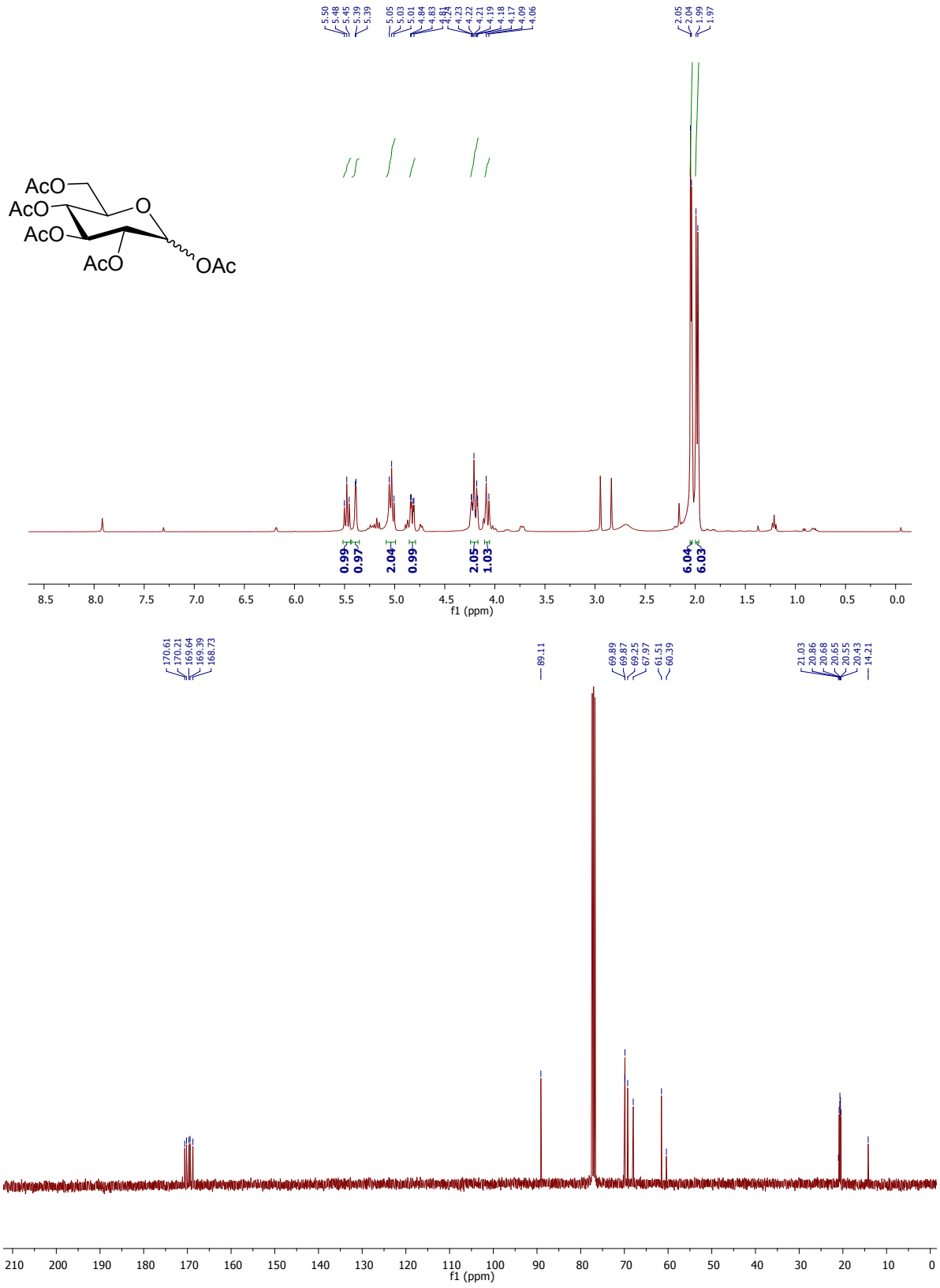


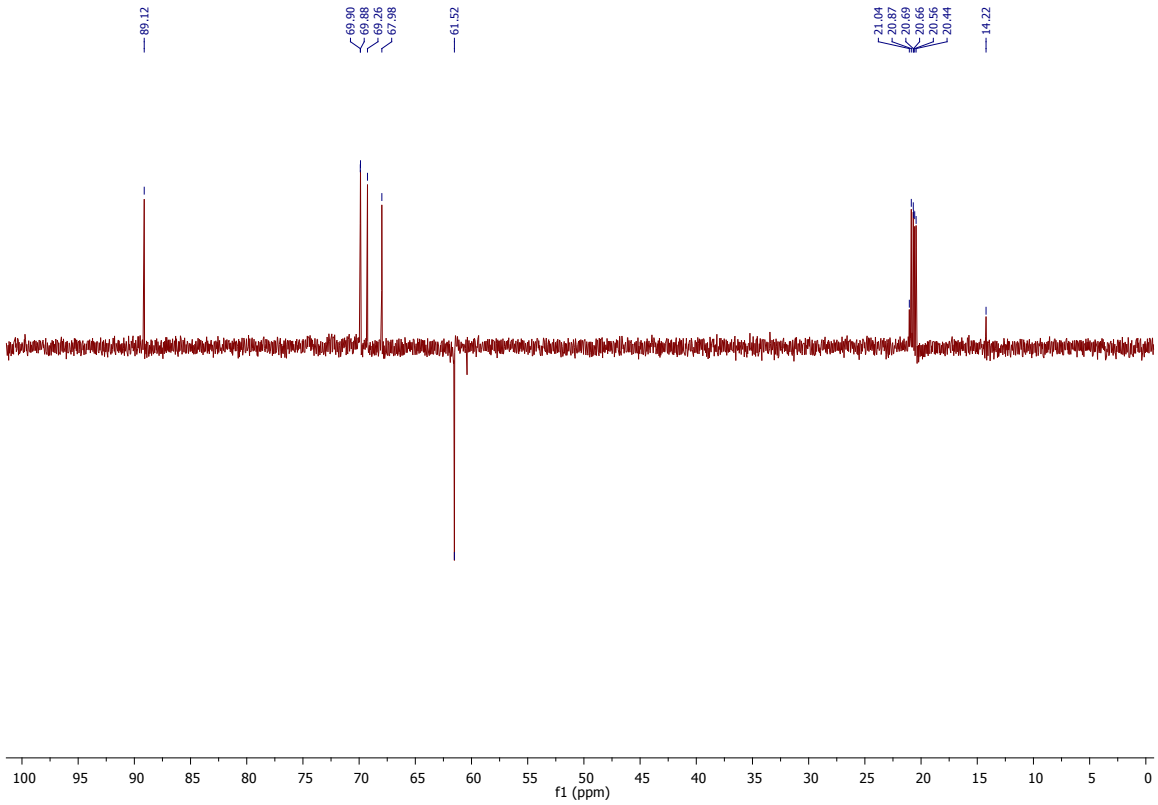


^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 5a ($CDCl_3$)

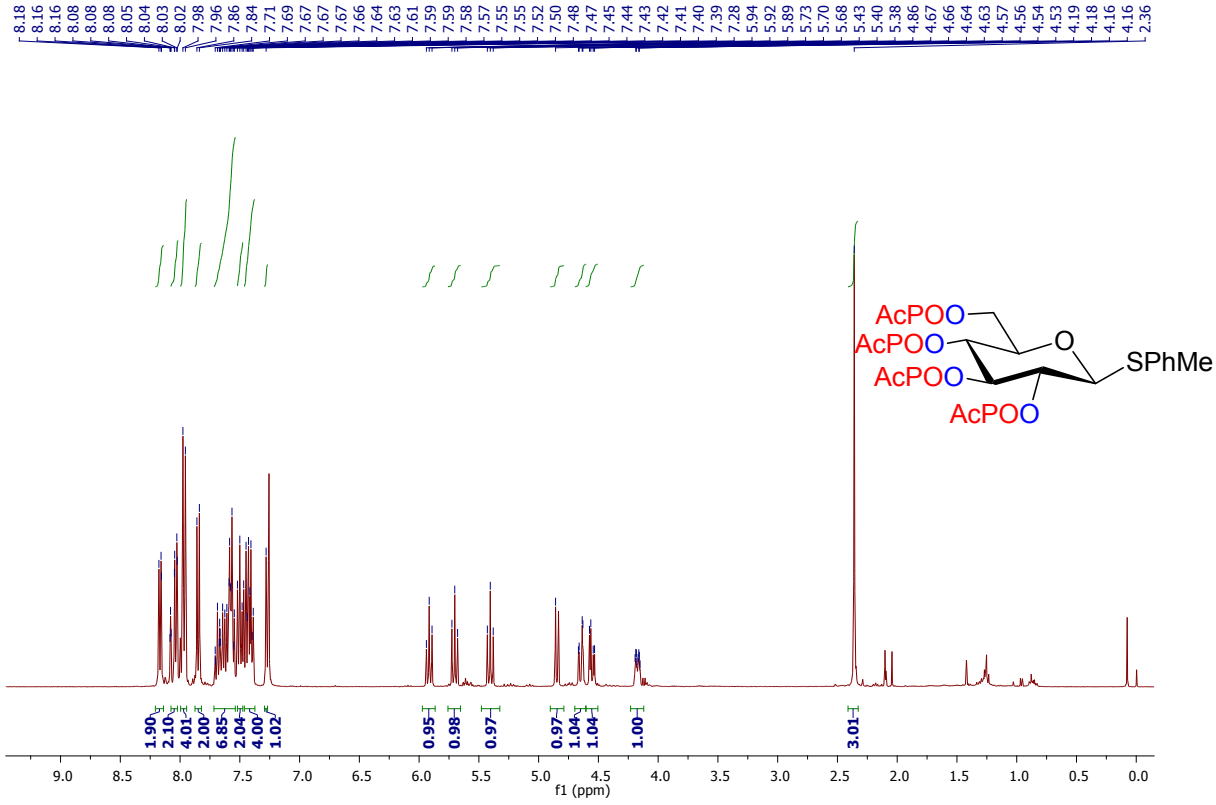


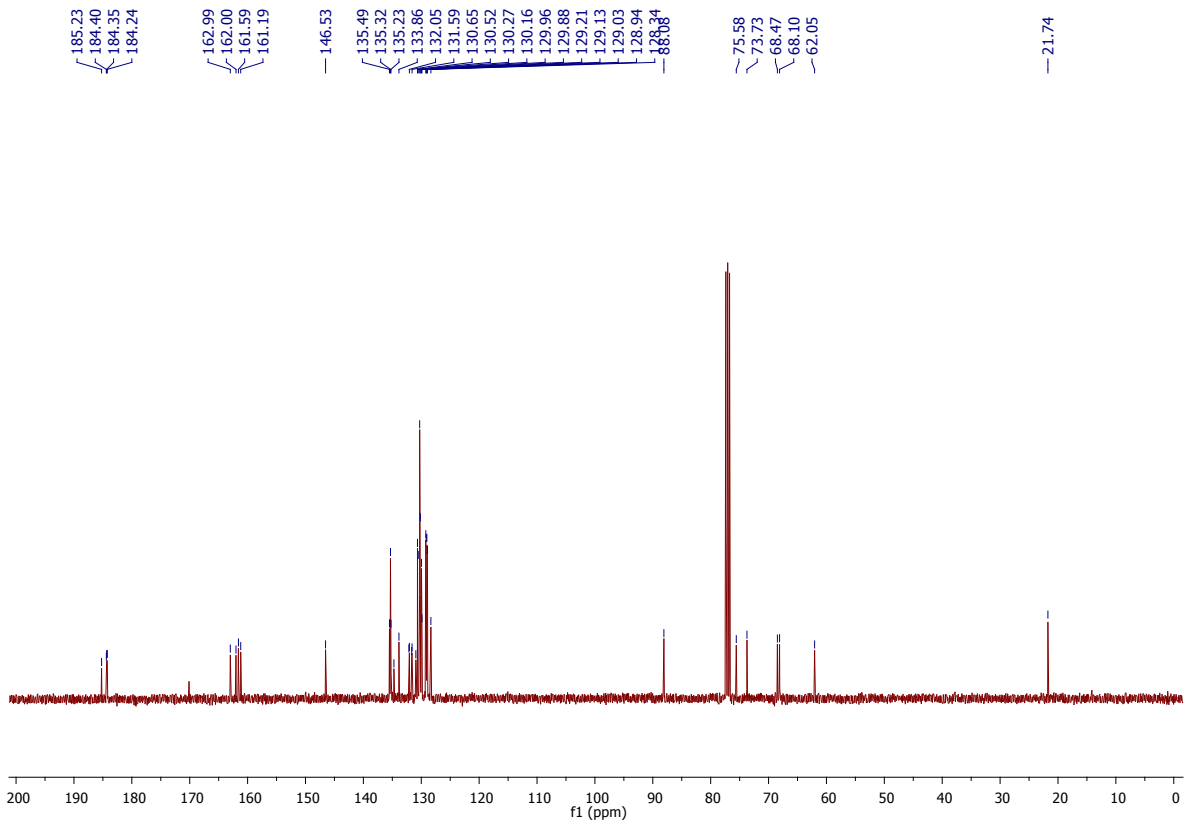
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 5b ($CDCl_3$)

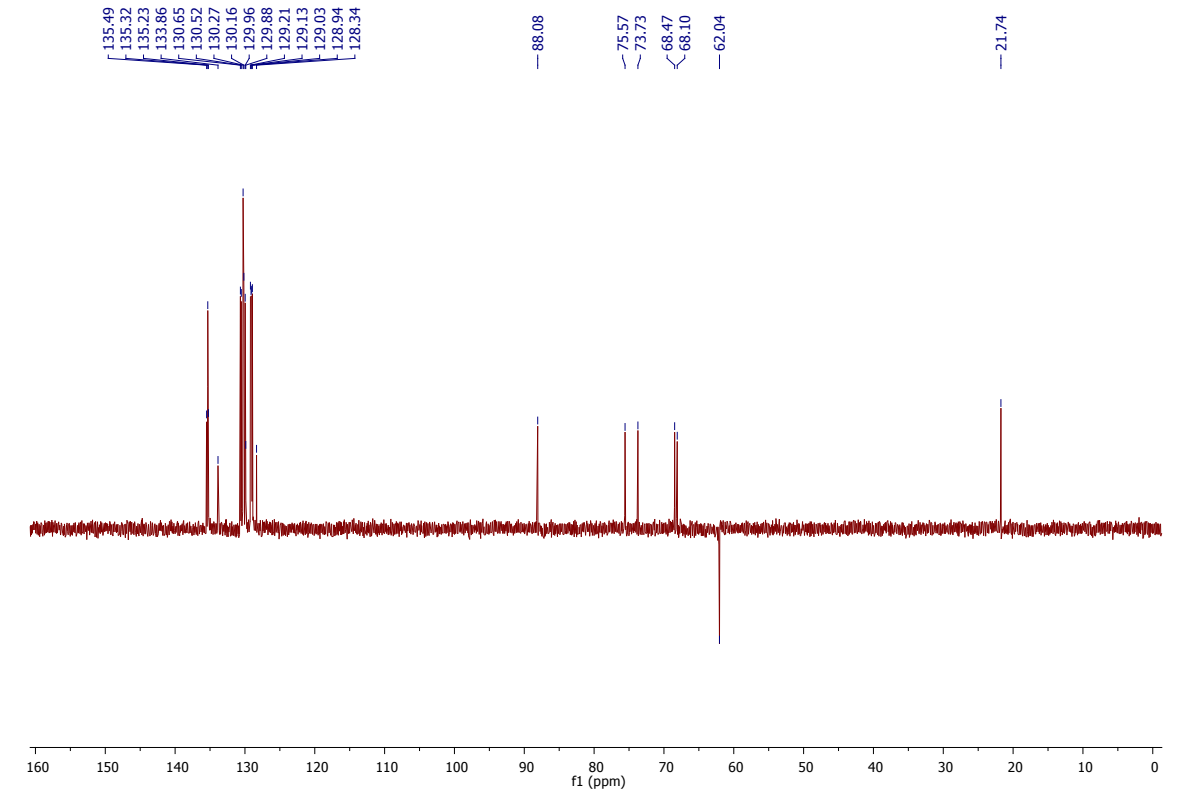




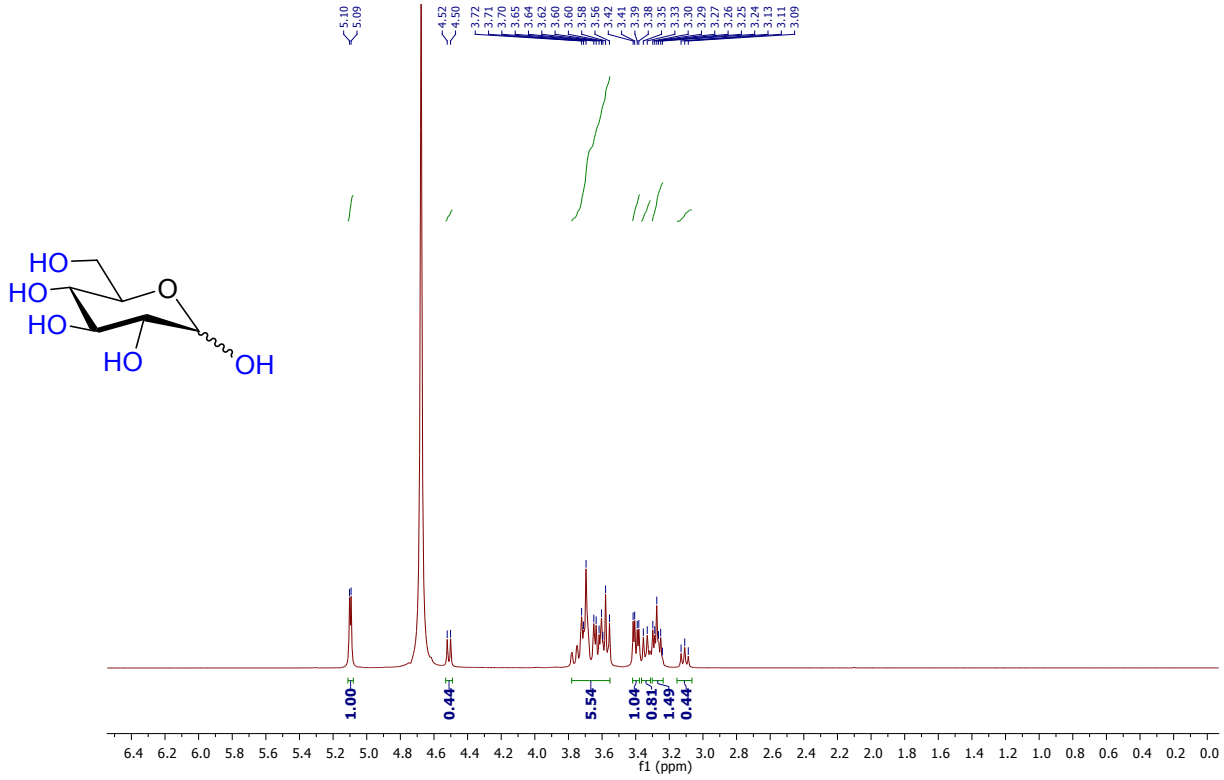
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 5c ($CDCl_3$)



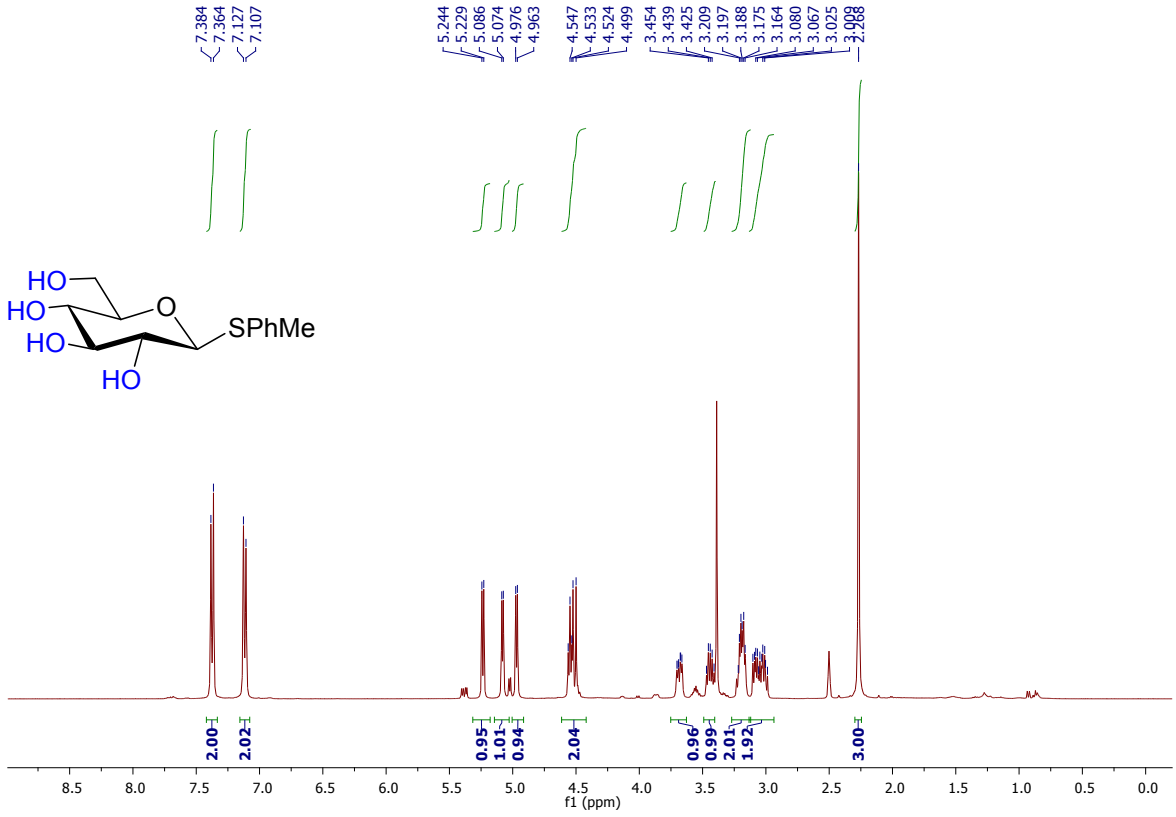

185.23
184.40
184.35
184.24
162.99
162.00
161.59
161.19
146.53
135.49
135.32
135.23
133.86
132.05
131.59
130.65
130.52
130.27
130.16
129.96
129.88
129.21
129.13
129.03
128.94
128.34
88.08
75.58
73.73
68.47
68.10
62.05
21.74
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

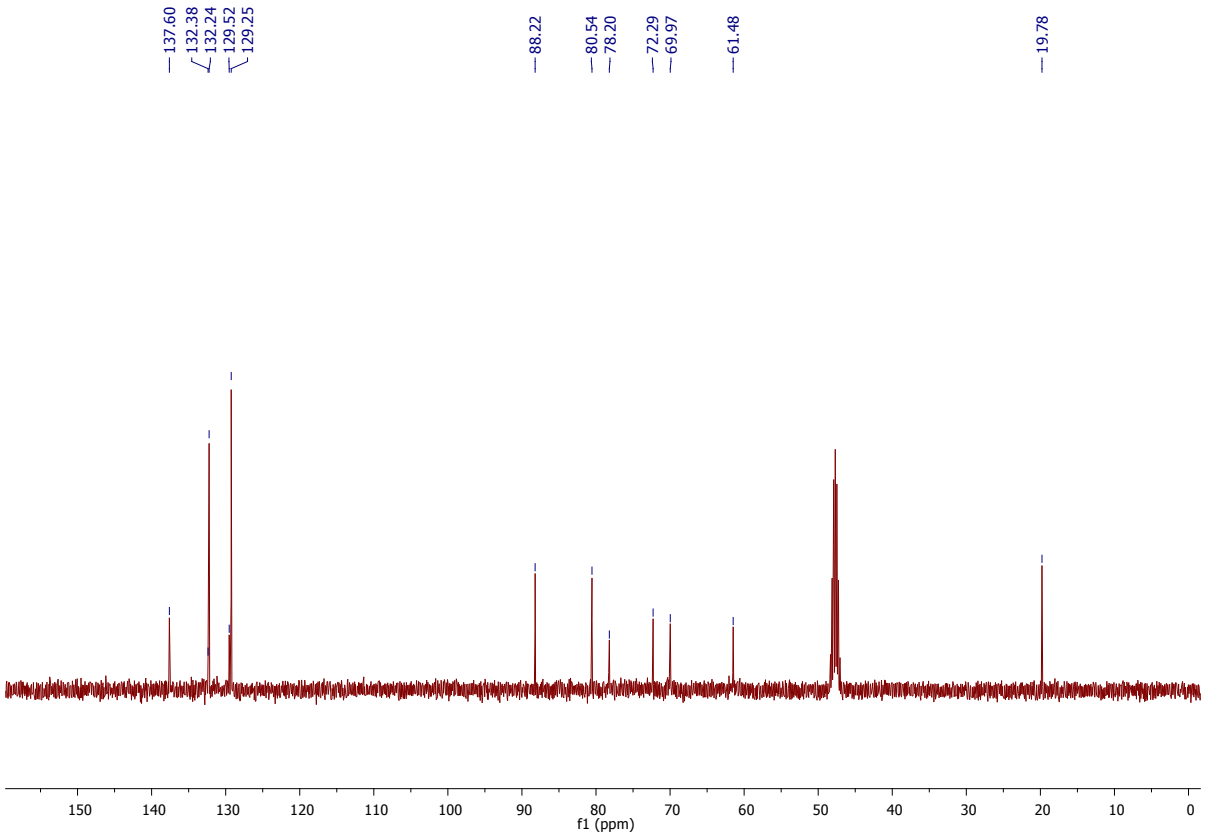

135.49
135.32
135.23
133.86
130.65
130.52
130.27
130.16
129.96
129.88
129.21
129.13
129.03
128.94
128.34
88.08
75.57
73.73
68.47
68.10
62.04
21.74
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

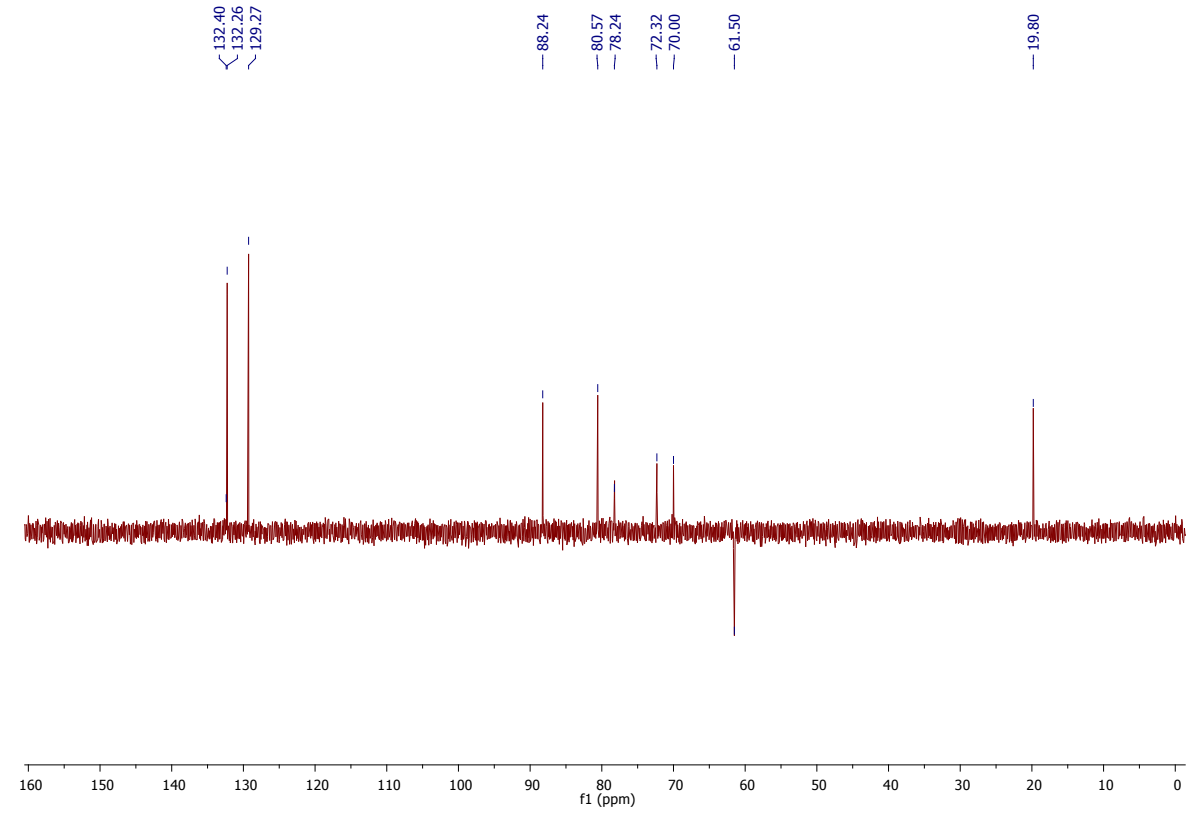
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 6a (D_2O)



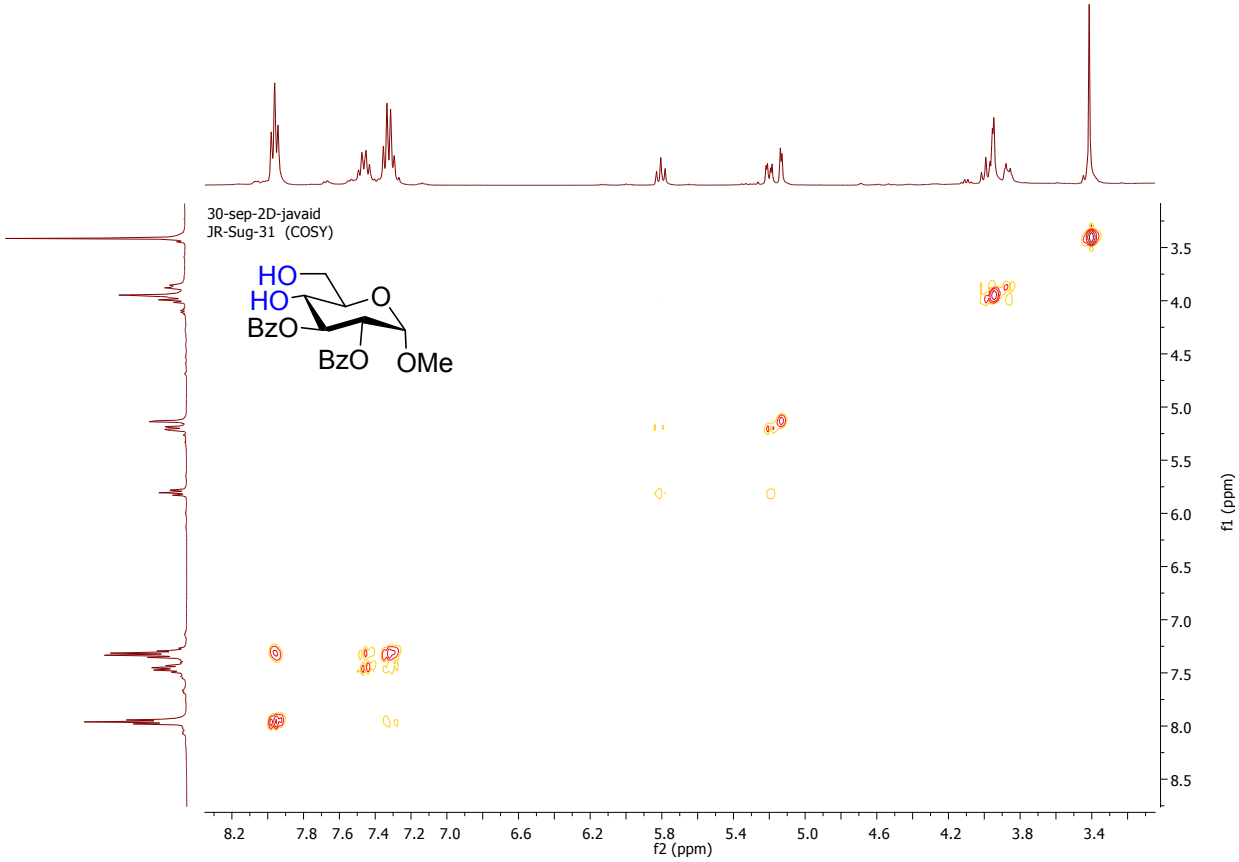
^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra of 6b ($CDCl_3$)

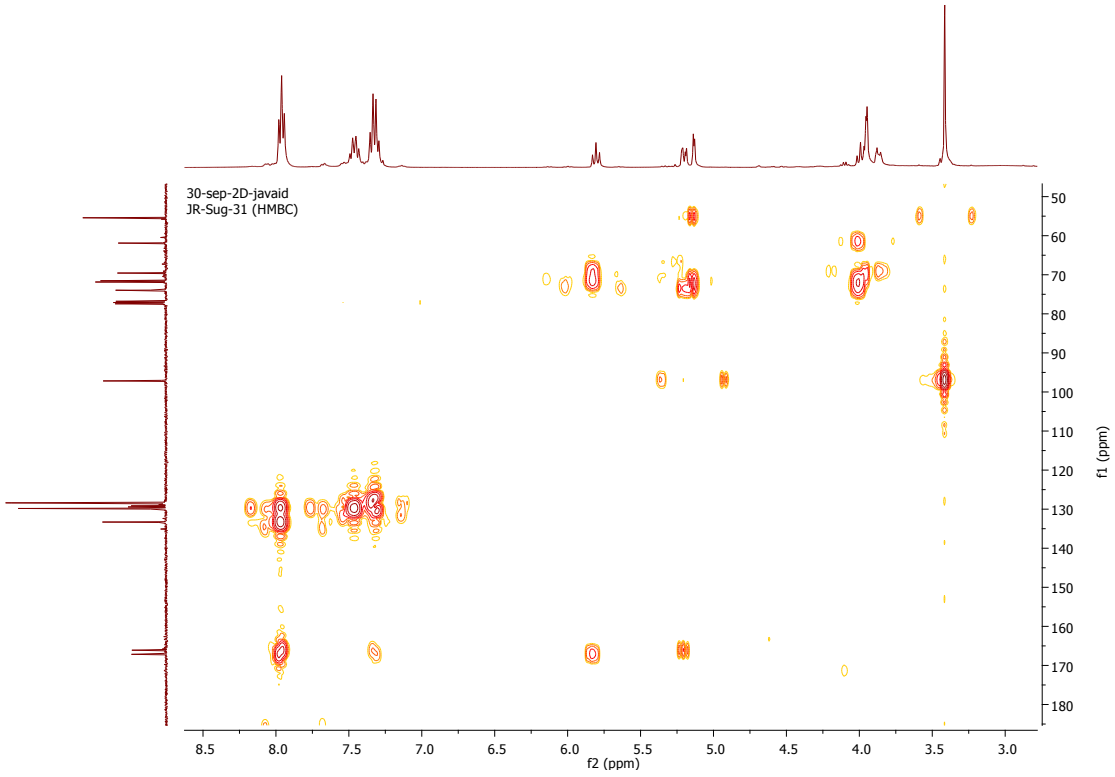


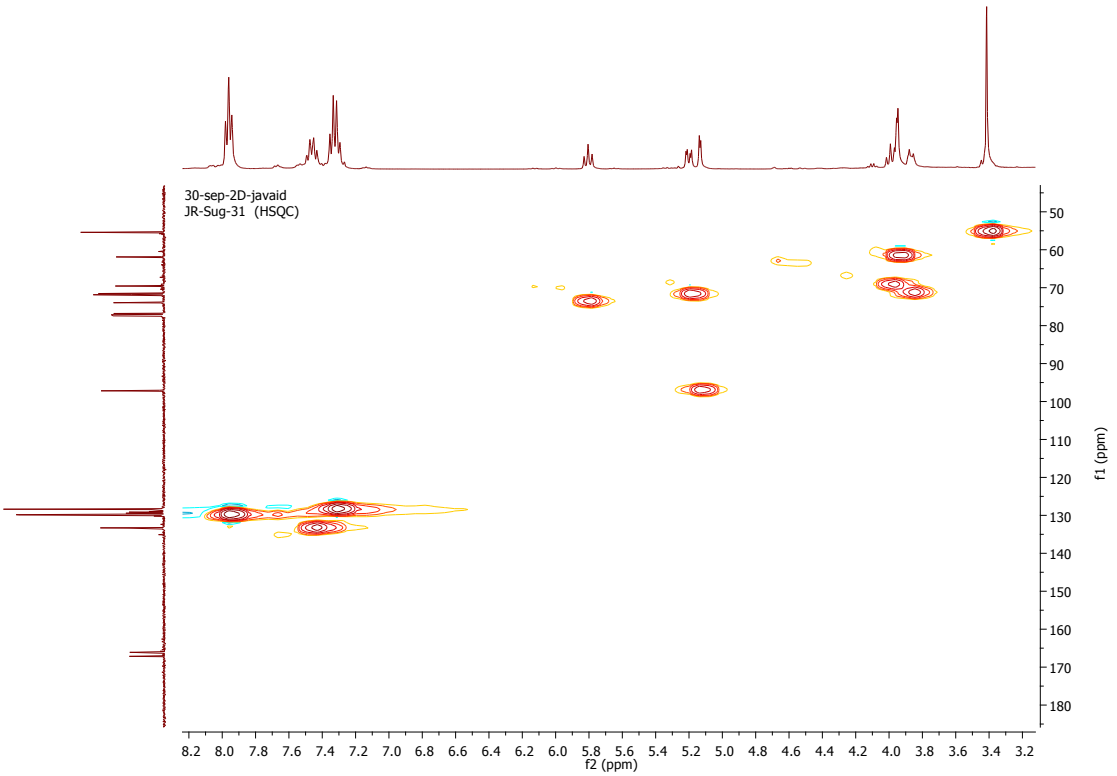

137.60
132.38
132.24
129.52
129.25
88.22
80.54
78.20
72.29
69.97
61.48
19.78
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


132.40
132.26
129.27
88.24
80.57
78.24
72.32
70.00
61.50
19.80
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

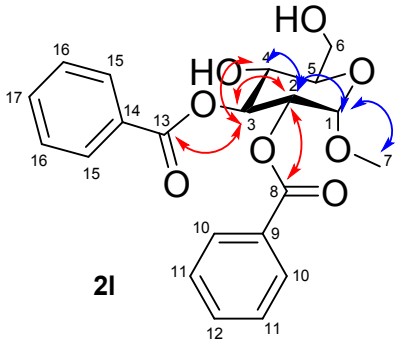
I. 2D Spectra of Compound **2l (COSY, HMBC and HSQC)**







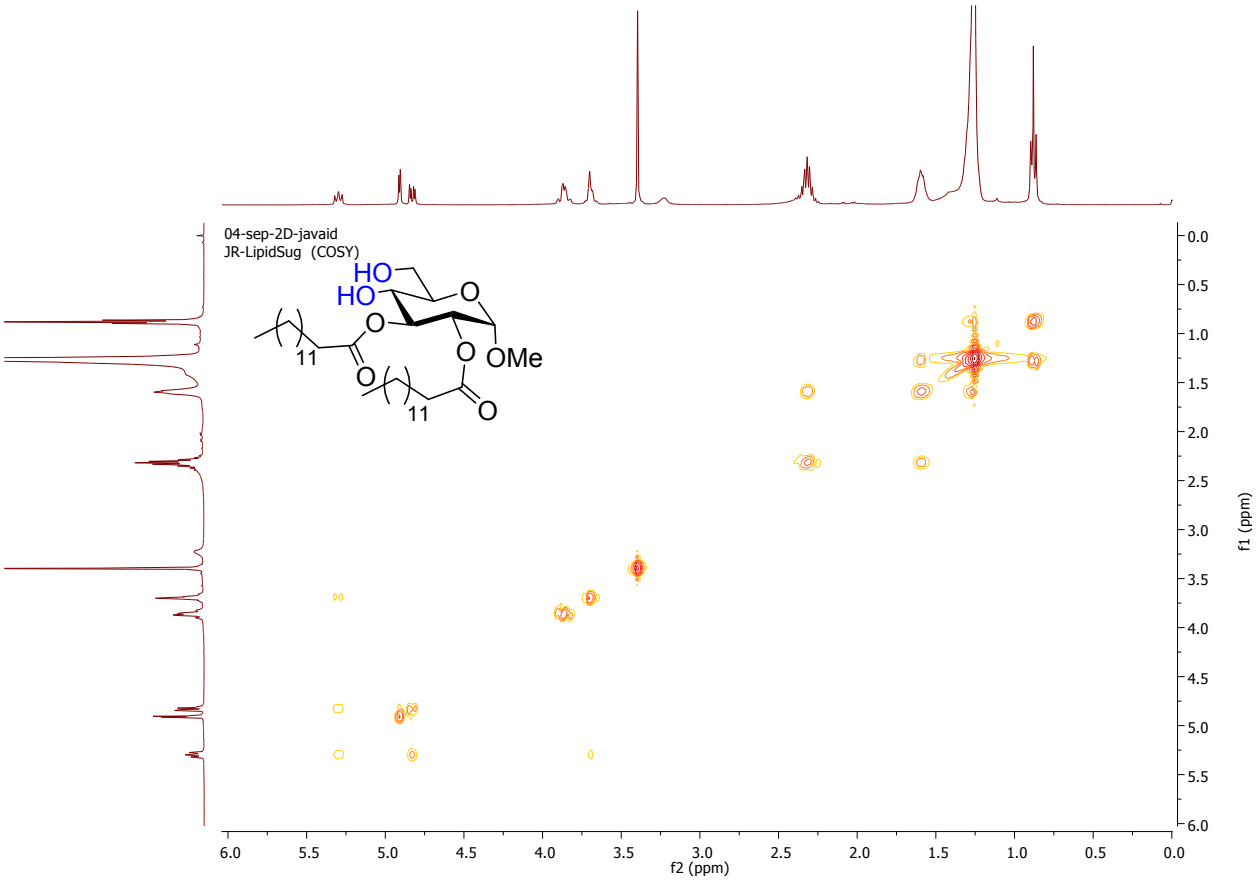
Summary of ^{1}H, ^{13}C, HSQC and HMBC Correlations observed for the Compound **2l** in $CDCl_3$ (Most important correlations are shown only)

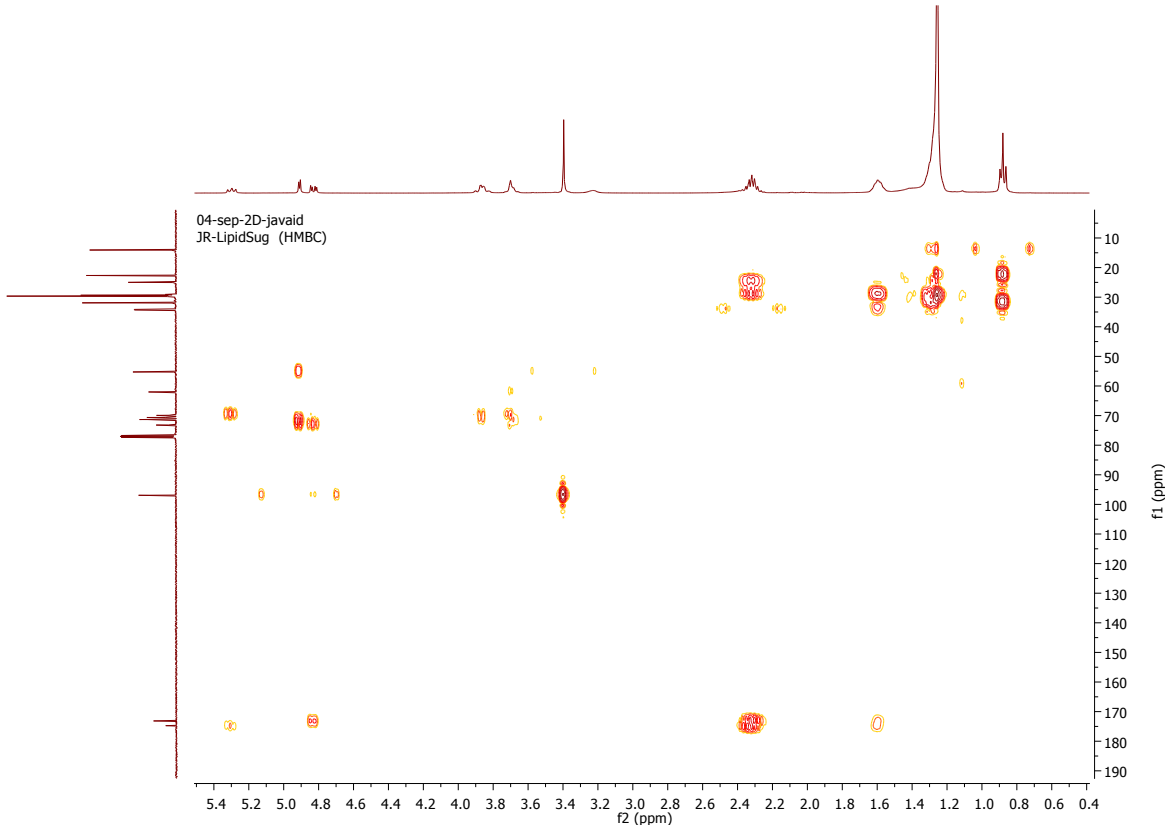


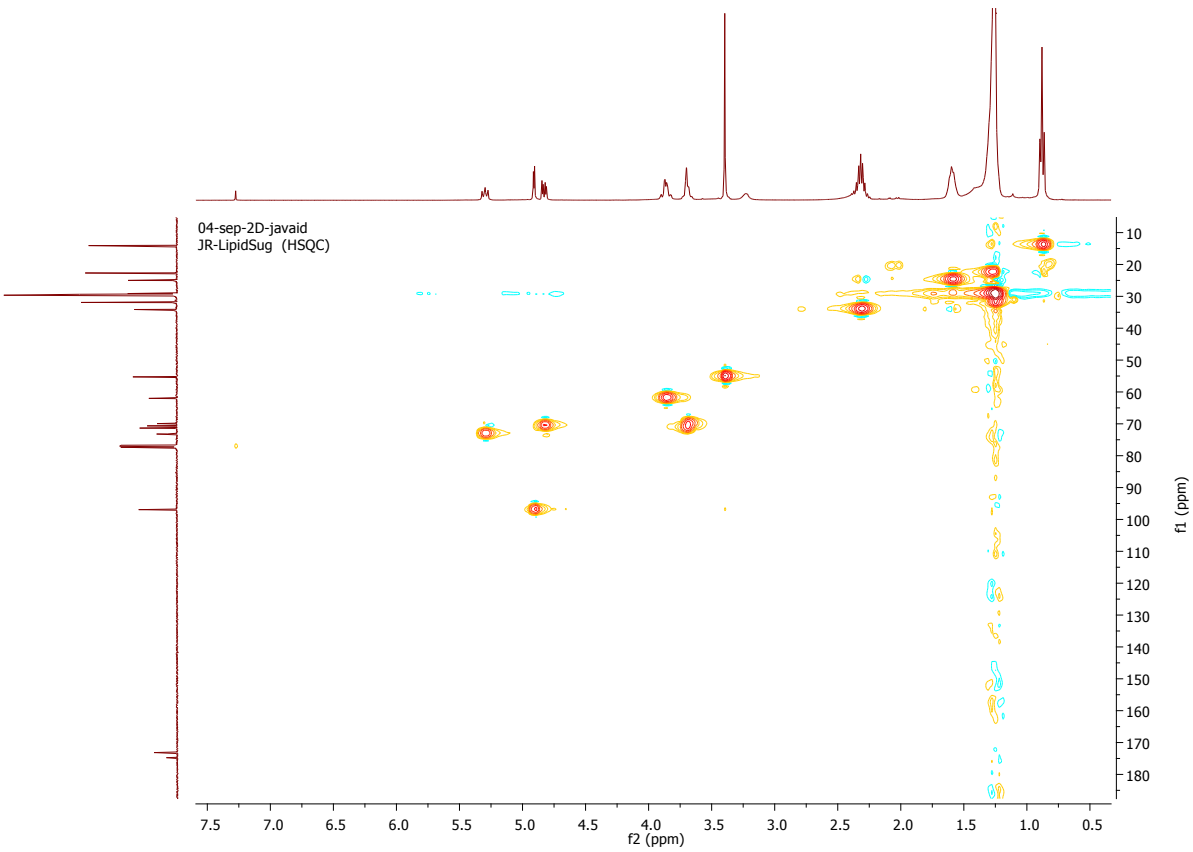
Position	δC	δH	HMBC Correlations
1	97.17	5.14	C-2, C-3, C-4, C-5, C-7
2	71.85	5.20	C-1, C3, C-4, C-5, C-8 (C=O)
3	73.96	5.81	C-2, C-4, C-13 (C=O)
4	71.54	3.99	C-2, C-3, C-5, C-6
5	69.56	3.86	C-2, C-3, C-4,
6	61.89	3.95	C-2, C-3, C-4, C-5,
7	55.41	3.41	C-1
8	166.10		
9	133.35		
10	129.43	7.32	C-9, C-11, C-12,

11	129.89	7.96	C-8, C-9, C-10, C-12
12	128.40	7.46	C-9, C-10, C-11,
13	167.16		
14	133.30		
15	129.15	7.32	C-14, C-16, C-17
16	129.82	7.96	C-14, C-15, C-17
17	128.38	7.46	C-16, C-14, C-15

J. 2D Spectra of Compound **4a (COSY, HMBC and HSQC)**

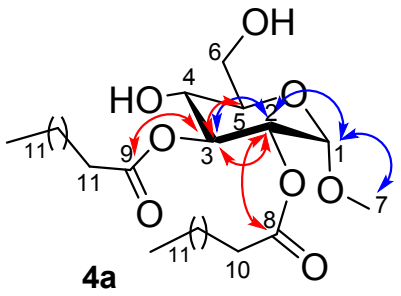



04-sep-2D-javaid
JR-LipidSug (HMBC)
f2 (ppm)
f1 (ppm)


04-sep-2D-javaid
JR-LipidSug (HSQC)
f2 (ppm)
f1 (ppm)

Summary of ^{1}H, ^{13}C, HSQC and HMBC Correlations observed for the Compound **4a** in $CDCl_3$ (Most important correlations are shown only)

Position	δC	δH	HMBC Correlations
1	96.92	4.90	C-2, C-3, C-4, C-5, C-7
2	71.33	4.82	C-1, C-3, C-4, C-5, C-8(C=O)
3	73.31	5.30	C-1, C-2, C-4, C-5, C-9(C=O)
4	70.60	3.69	C-2, C-3, C-5, C-6
5	70.04	3.67	C-2, C-3, C-4
6	62.08	3.86	C-2, C-3, C-4, C-5
7	55.27	3.38	C-1
8	174.82		
9	173.12		



4a